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THE MATHEMATICAL THEORY OF A NEW RELATIVITY

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CHAPTER VI

Criticisms Answered

SECTION I

INTRODUCTION

Considerable misapprehension has been unfortunately aroused that the existence of gravitons is the essential foundation of my Theory. Although for mathematical facilities attention was concentrated in Chapter I on the path of a particle, it was clearly pointed out on page 5, paragraph 2, that the assumption of the existence of gravitons was not at all necessary for the theory. The same point was again emphasised on pages 219, 229 and 261 in the later chapters. But owing to the frequent reference to gravitons, the main idea was somewhat obscured. No doubt the *Physical Theory* involved the assumption that gravitational influence is propagated outwards in all directions equally, and thus necessarily led to a diminution of intensity in the ratio of the inverse square of the distance. Again if the attractive influence emanates from every mass, then it must necessarily be proportional to the mass of the influencing body, and if the influence is mutual, then it must also be proportional to the mass of the influenced body. But the only solitary assumption which is necessary for my Mathematical Theory is that, quite regardless of any physical

theory of gravitation and quite irrespective of the way in which gravitational attraction might be caused, *the gravitational influence is propagated on all sides from a body of mass outwards with a finite velocity.* From this one single assumption the rest of the results can be deduced purely mathematically. That the influence of gravitation should be propagated outwards from the Sun is a natural assumption, for if the influence were not propagated from the Sun towards the planet, but in the opposite direction, such influence would never reach the planet at all. The finiteness of the velocity of propagation necessitates the compounding of the velocities, producing the well-known aberration effect. The finiteness of the velocity also involves a change in frequency if the two bodies are relatively in motion. These necessary results are in themselves quite sufficient for the mathematical analysis in Chapters I and II.

Similarly, in Chapter III the assumption that light consists of swarms of rotating particles was quite sufficient to explain that a part of the apparent recessional velocity of nebulæ must be spurious, as light would be reddened as it passes through space. Even for Chapter IV it was not necessary to assume the existence of gravitons. Section V in particular avoided such an assumption. All that was necessary for this chapter was that some fine particles, maybe light corpuscles only or even heavier particles like electrons and even atoms and molecules, are thrown off from an outer layer in all directions. The effect of the motion of a nebula could then be sufficient to produce a difference in the losses of momenta in the front and at the rear, resulting in a net acceleration in the direction of motion, which will explain the recessional velocity proportional to distance after a sufficient distance has been covered.

As is observed for light, it was assumed that these material particles emerge from a moving nebula with constant velocity in space, that is to say, their spacial velocity is independent of the velocity of the source; and a physical explanation of it was also offered. This is just the assumption that is made in Relativity, without the additional assumption that this constant velocity in space is also a constant relative velocity, no matter howsoever fast bodies may be moving. But even this assumption is not essential for the theory. All that is necessary to assume is that particles that emerge are *not wholly* carried along by their source, that is to say, they do not in addition to their own intrinsic velocity possess the whole of the velocity of the source. So long as there is a residual difference between the velocity with which they are partially carried along and the velocity of the source, there would be a balance of momentum left which would result in a net acceleration in the

direction of motion. Thus by merely denying that light particles are wholly carried along by their source, one can arrive at the same mathematical result as in Section V. The constant co-efficient would then be of a smaller value, helping to prolong the ages of the nebulæ, and making the life of our galactic system longer than it appears, thus satisfying the needs of evolution better.

Four more chapters are submitted now. In Chapter VI certain published criticisms have been answered. Hamilton's supposition that my theory was similar to Lesage's or that it must founder on the same rock as Laplace's theory, has been refuted; and it is pointed out how the theory steers clear of that rock. It is claimed that this theory is the only known theory which can explain the positive value for increases in the eccentricities of the Earth, Mars and Venus, as observed by Newcomb. Some reasons have been given for not accepting Satyendra Ray's suggestion. A short note has been added on A. C. Banerji's remarks, and sundry other points also have been noted.

In Chapter VII the claim of Relativity that only relative velocities can be measured, and not absolute velocities, is examined, and it is shown that relative velocity as measured has no meaning, unless it is also specified how measured, as different methods of measuring relative velocities give entirely different results. It is just as impossible to measure exactly the actual relative velocity, *i.e.*, the difference between two absolute velocities, as the absolute velocities themselves. Newton's value is true to the first order term, and Einstein's to the second order terms. For higher approximations the relative velocity is a function of the actual velocities and not only of their difference.

Chapter VIII deals with the retardation of gravitational influence and points out certain further corrections which must be made to the Newtonian law of gravitation for more accurate results.

Chapter IX deals with the effect of a resisting medium, which would greatly nullify the effect of the accelerated motion and thereby reduce the perturbations.

The Appendix points out that the special shift in the light from the centre of the Sun's disk is unreliable, and a different value is calculated for the shift in the light from the limb.

It will appear that Newton's principles have not failed, but that his Mechanics requires several necessary corrections, which make the equations of motion highly complex, yielding more accurate results with higher approximations. On the other hand, the assumptions in Einstein's Relativity are mere approximations, and give tolerably good

results in practice, but not being rigorously true, the philosophy based thereon is a failure, making its results unintelligible to a three-dimensional being.

I must again express my gratitude to Mr. A. N. Chatterji, M.Sc., for his great kindness in helping me in checking the mathematical processes and to Dr. D. S. Kothari, D.Sc., Ph.D., for making valuable suggestions.

SECTION II

D. R. HAMILTON'S CRITICISMS

D. R. Hamilton, professedly with the "assistance" of H. P. Robertson, of the Princeton University, to which Einstein himself now belongs, has published a criticism of my Theory.[1] The criticism is not directed against anything published by me, but suggests certain untoward results that he supposes would follow from the finiteness of the velocity of gravitation in my Theory. I propose to meet his objections *seriatim* :—

1. He thinks that I have based my theory of gravitation on "gravitons."

As pointed out in the preceding section, this is a clear misapprehension so far as my Mathematical Theory is concerned. I maintain that I have made only *one solitary assumption and no more, viz., that the influence of gravitation travels with a finite and not infinite velocity.* My equations are mere mathematical deductions from this one single assumption.

2. He considers that my hypothesis of gravitons "is essentially the same as that put forward by Le Sage in 1764 as an explanation of gravitation."

Now my physical theory of gravitation is a theory of *emission* of matter and not of impinging or absorption.[2]

On the other hand, Le Sage's theory was that space is full of small corpuscles moving in all directions which hit material bodies and are thrown back.[3] Accordingly, one body partially shields another body, causing a net resultant effect of attraction. But the force, although inversely proportional to the square of the distance, would not be proportional to the masses, but would instead depend on the dimensions of the bodies. Clerk Maxwell showed that even the inference of the proportionality to dimensions was incorrect as although some corpuscles would

be intercepted by one body, others after reflection from it would hit the other body which would not otherwise do so. As suggested by Lorentz, the theory can be somewhat saved by further assuming that the corpuscles are wholly or partially absorbed by matter, but then the theory loses its simplicity.[4]

There is hardly any identity between the two. Further, as the existence of gravitons is not at all necessary for my Mathematical Theory, no question of any similarity with Le Sage's theory arises. The analogy disappears altogether.

3. He considers that my theory does not remove the objection to "Laplace's mathematically analogous theory."

Laplace's theory[5] was based on the idea that gravitational attraction was produced by the impulse of a fluid on the centre of the attracted body. No doubt he considered the possibility of a finite velocity of gravitation, but his theory led to the propagation of gravitational influence being directed from the influenced body to the influencing body, with the result that the extra-tangential force caused a *retardation* of motion. He started with the simple Newtonian law, and not only neglected the small deficiency in the component along the radius vector, but also quite arbitrarily assumed that the surplus component along the tangent was nearly the same as that along the transversal. These assumptions made the integrations quite easy. But his result of a retarded tangential motion, although it had no effect on the longitude of the perihelion, introduced large secular perturbations in the semi-major axis, the eccentricity and the mean longitude of the planet in the orbit, which would not tally with observations unless the velocity of gravitation were 6×10^{6} times that of light in the case of Mercury. The idea of any velocity commensurable with that of light had therefore perforce to be abandoned. Neither Laplace nor Tisserand could think of a resisting medium as an explanation, because the equations led to a retardation, and a resisting medium would have made the result much worse. Laplace's equations did not yield any formula tallying with the observed advance of the perihelion of a planet. The gravitational deflection of light and the red shift of the spectral lines were not considered by them at all, and indeed were not known at the time.

My equations are derived from the analogy of the well-known principle of retarded potential in an electric attraction; and the gravitational influence is propagated naturally from the influencing body outward to the influenced body. The equations take account of the reduced effect due to the relative motion of the bodies and so contain additional

terms, which render the equations extremely complex and incapable of exact solution. Only a few solutions by successive approximations, obtained by omitting higher powers, have been so far published by me. But my equations definitely lead to an *acceleration* and not retardation of motion.

4. He acknowledges that the changed magnitude of the attractive force as deduced by me has "the net result of introducing an advance of the perihelion close to the desired value in the case of Mercury." It is also gratifying that there are no adverse remarks regarding my formulæ for the deflection of light and the spectral shift. These three are the chief results on which the claims of General Relativity are based.

5. He directs his criticisms against the resultant perturbations in the semi-major axis and the eccentricity only. Thus the results arrived at by me in Chapter I, much less those in Chapter II, are not challenged; and a premature attack is delivered in the form of an objection made in advance to what is to follow in a later chapter.

6. With regard to the perturbations in the semi-major axis and eccentricity, he suggests that I "had apparently not carried out the calculations." This remark is astonishing as I had at considerable length worked out the exact values of these perturbations in Chapter I, Section XII, pp. 20—24. Indeed in finding the values of these perturbations I had even ventured to claim an originality of treatment by saying on p. 24: "The method of treating the disturbed elliptic motion as being due to small additional forces which has been followed in this section is not known to have been adopted previously." The reason why the further consideration of these perturbations was intentionally postponed to a later chapter was that I was first concerned with offering substitutes for the three main formulæ of General Relativity, which it was commonly believed could not be deduced from Newtonian Mechanics.

7. He says that the absurd size of my perturbations can be realized if the cumulative effect of yearly increases in Mercury's eccentricity be considered.

Simple calculations based on yearly increases for a large number of revolutions are obviously fallacious. The solutions of my equations have been obtained by me after eliminating the time t. The curve thus found represents a geometrical picture of the orbit, and that too only within the limits of the approximations. It does not at all profess to give the whole history of the revolutions of a planet for a long period. The fallacy underlying the contrary assumption becomes at once apparent when similar increases are applied to Einstein's equations (8·2)

and (8·3) on page 12 which would then assume that $\cos \epsilon = 1$ and $\sin \epsilon = \epsilon = \frac{3\mu^2}{c^2h^2}(2n\pi + \theta)$. These break down when n is large. The obvious explanation is that the geometrical shape of the orbit is one thing, and the whole history through its spiral path is quite another.

8. Quoting Laplace, he remarks "the resulting tangential acceleration (retardation?) of the planets had no effect on the longitude of perihelion, but introduced secular perturbations in the semi-major axis and eccentricity of the orbit and in the mean longitude of the planet in the orbit." On the authority of Jenneck and Chazy, he concludes that the velocity of gravitation would have to be extremely large ranging from 6×10^4 times the velocity of light in the case of Mars, to 2×10^6 times in the case of the Earth. He argues that otherwise Mercury would leave the solar system in about 300 years from now, and that if the velocity be not so large, the advance of perihelion would be negligible.

It will be shown later that the force of gravitation along the shifted direction has a large component, nearly equal to Newton's value, along the radius vector, which would account for Kepler's perfect ellipse; and it has a further small component along the radius vector and another slightly larger component, of the order of about 1/1000 in the case of the earth, transversely to the radius vector. These last two can be resolved into components along the tangent and the normal respectively. The normal component causes only periodic fluctuations, its net result on the semi-major axis and the eccentricity for a complete revolution is nil. It is only the tangential component, which causes acceleration of motion, tending to increase the semi-major axis and the eccentricity. Now Laplace and Tisserand had no explanation for the perturbations caused by the tangential retardation except the largeness of the velocity of gravitation which broke down the theory. But my Theory leads to a tangential acceleration and not retardation; the tangential acceleration can be counteracted by the retardation caused by the resisting medium, which acts tangentially in the opposite direction, and while producing a null effect on the advance of the perihelion reduces the dreaded perturbations.

9. He admits that the sign predicted by my formula in the case of the eccentricities of Venus, Earth and Mars agrees with Newcomb's observations, but points out that the discrepancy in Mercury's eccentricity between Newtonian theory and observations is of opposite sign.

Now Laplace's theory could not offer any explanation of such a change of sign. And neither Newton's nor Einstein's theory can explain

an increase of semi-major axis and eccentricity for Venus, Earth and Mars, nor a decrease in the case of Mercury. But in my Theory, the effect of resistance being small for these larger planets, the sign remains unaltered; but as Mercury is closer to the Sun and the resistance larger, the retardation due to the resistance just overcomes the accelerations of motion, and the discrepancy changes sign. In the case of Encke's comet, which passes closer still, the resistance is so much that it actually causes a marked shortening of the period.

He confidently asserts that my Theory, "in so far as it relates to gravitation, would seem, then, to founder on the same rock as Laplace's mathematically analogous theory."

The *acceleration* produced in my Theory, in direct contrast with the *retardation* produced in Laplace's theory, makes an important difference, which saves my Theory from that fate.

10. D. R. Hamilton is obviously not aware that it has been noticed by Lorentz[6] and A. S. Eddington[7] that Laplace was quite wrong in concluding that unless the velocity of gravitation was enormously large, the tangential component would cause much larger perturbations than are actually observed. Indeed, on Laplace's own theory the effect of the first order term would be wholly compensated even if the velocity of gravitation is equal to the velocity of light, provided the retarded potential is taken into account. The difficulty will, however, remain that Laplace's theory would still fail to give the value for the advance of the perihelion, nor would it explain the spectral shift of light from the Sun.

11. I may here add that $-\frac{\mu}{r^2}-\frac{3\mu h^2}{D^2}\frac{1}{r^2}$ where h is twice the area described per second even for light and $D=c$, is an empirical law of gravitation which gives all the required results without causing any difficulty. It causes no perturbations in the major axis and the eccentricity, produces an advance of perihelion $=\frac{6\pi\mu^2}{D^2h^2}$ and the spectral shift from the centre $=\frac{\mu}{a}$. The deflection of light $=-\frac{\mu}{c^2R}\int_{-\pi/2}^{\pi/2}(1+3\cos^2\theta)\,d\theta$ $=-\frac{2\mu}{c^2R}\left(1+\frac{\pi}{2}\right)=2''{\cdot}24$ tallying with Freundlich's mean value $2''{\cdot}20\pm 10$.

SECTION III

SATYENDRA RAY'S SUGGESTION

1. Some time after the publication of the first two chapters of my Theory, Satyendra Ray of the Lucknow University suggested to me that

(a) instead of assuming that matter is emitting gravitons, I might assume that it is absorbing them and (b) that the algebraic quantity D in my equations, instead of being taken as of positive sign, might be taken to have a negative sign. (c). He thought that this change of sign would not materially alter the results, as it is only D^2 and not D that occurs in the main formulæ. (d) Before the publication of Chapters III and IV, when I had explained to him only "orally and summarily" the acceleration produced on an isolated moving nebula by its own emission, he inferred that even on my Theory "a moving body uniformly radiating in every direction experiences a force tending to stop its motion. . . . The motion itself generates a friction of motion which tends to stop it," in conformity with classical astronomers like Lagrange.

(1) The idea that gravitons are flying about in space and enter into and are absorbed by matter is exactly identical with that of Le Sage, as modified by Lorentz, already discussed in the preceding section. It is therefore not a new idea. The first objections to it are the same as there pointed out. Other objections are that if gravitons are emitted by matter at intervals and have the same velocity, they can travel with fixed spacing; but if they already exist in space at random, they cannot have any uniform spacing; also the theory involves a flow of matter from a lower material potential to a higher potential where there is already concentration, contrary to what we actually observe in radiation.

(2) The idea that D should be given a negative sign and therefore measured in the opposite direction is identical with Laplace's theory discussed in the preceding section, and is also not a new idea. The theory broke down because the large secular perturbations in the semi-major axis, the eccentricity and the mean longitude of the planet could not be explained by Laplace. The large decreases in these elements, which that theory produced, are not at all observed. As D. R. Hamilton has pointed out, if to get over this difficulty the value of D is increased sufficiently, the advance of perihelion would, contrary to observation, be negligible. Ray cannot therefore avoid the horns of Hamilton's dilemma. If the effect of the retarded potential is taken into account, then the value of the advance of the perihelion is very largely diminished.

(3) It is not quite accurate to say that only the second power of D occurs in the principal equations and therefore it matters little whether D is positive or negative. A negative D would alter the sign throughout.

If the propagation is in the direction opposite to v, the factor on p. 8 will be $(1+v/D)^3$ and the sign of D would be changed both in (5·4)

and (5·6). Therefore there would be a change in the value of the advance of the perihelion in (11·13). It would also alter the sign of $\triangle a$ in (12·2) and (12·3) and therefore also in (12·4); and similarly of $\triangle e$ in (12·6) and (12·7) and therefore also in (12·8) in which the first power of D occurs. These give decreases of the order 10^{-4}, whereas increases of the order 10^{-8} are mostly observed, falsifying a negative D.

(4) After the publication of Chapter IV, the last point vanishes. The effect is there shown to be an acceleration and not retardation. But he still maintains that γ in (20·1) may be negative. If so, the equation would produce a shrinking universe instead of an expanding one, which is contrary to observation. The utility of a theory lies in its concordance with observation; if that does not exist the theory is useless.

(5) The conception of æther particles flying about in space, hitting protons and being absorbed by them was put forward by Tombrock of Holland in his Chemische Stofferklarung (1933). Gravitation was assumed to be caused by pressure of æther particles from all sides. A single body is held in equilibrium, but the presence of another body acts as a screen. The difference in the momenta on the outer and the inner sides of a body will result in motion towards the second body, appearing as gravitation. As pointed out by me in my Introduction to the English translation of his book by Jackson, the theory would lead to Newton's law of gravitation. The objection to it is that like Laplace's theory it leads to a velocity of gravitation in the opposite direction from the planet to the Sun causing the same difficulties.

2. The reasons why at present I cannot accept Ray's suggestion (already shown to be the same as that of Le Sage, Lorentz and Laplace) may be summarised as follows :—

(*a*) My mathematical theory is really independent of any physical theory of gravitation, and holds irrespective of the question whether gravitational effect is the result of emission or absorption of gravitons. I wish to keep my mathematical theory clear of any such commitment, and have based it simply on the propagation of gravitational influence from a body outward in all directions with a finite velocity.

(*b*) It is illogical to assume that the influence of gravitation is propagated from the influenced body towards the influencing body. If the influence of the Sun were propagated in a direction from the planet to the Sun, it will never reach the planet at all.

(*c*) D in my equations is an algebraical quantity and, mathematically speaking, can be both positive and negative. But I must reject a negative D, as that would lead to unexplained large secular perturbations

in the elements of the orbit, which are falsified by actual observations, both as to their sign as well as their magnitudes in the case of Venus, Earth and Mars.

(*d*) When the rotation of both the Sun and a planet are taken into account, the retarded gravitation would make the advance of the perihelion vanish almost completely.

(*e*) Laplace's theory curiously made the intensity of gravitational influence increase if a body were moving away from it, so that the value of the spectral shift on that view would be several times that of Einstein's.

(*f*) A negative D would make the nebulæ retard their motion, and would not explain their recession with a velocity proportional to their distances. What we would then have observed would be a shrinking and not an expanding universe.

I may add that if a negative D were found to accord better with observation, I would be only too happy to accept it. Although I cannot accept the idea that the influence of the gravitation of the Sun should have a velocity in the opposite direction, travelling from the planet towards the Sun, I would, ***provided*** it were not only dynamically sound, but also made to yield values of the advance of the perihelion and of the spectral shift tallying with observation, be prepared to adopt a modification of Laplace's theory, that even with a positive D, the gravitational effect on a moving body is obstructive, causing a slight retardation.

SECTION IV

A. C. BANERJI'S REMARKS

1. A. C. Banerji of the Allahabad University[8] has published some general remarks on my Theory. I am grateful to him for his "congratulating me on the accuracy in the mathematical working out of my Theory in which he could not find any flaw." I fully accept the tests which he has laid down for purposes of comparison, and claim that my Theory can stand them.

The Introduction explains that I have made only one solitary new assumption, *viz.*, the finiteness of the velocity of gravitation. His main criticism is that the emission of gravitons with constant velocities wholly along the radii is an extraordinary assumption inasmuch as cross-radial momentum is not taken account of. The answer is five-fold.

(1) The approximate constancy of the velocity of gravitons in space is exactly identical with the similar constancy of the velocity of light assumed in Relativity. The one is no more extraordinary than the other is. (2) The assumption that gravitons when they emerge have nearly a constant velocity necessarily involves the inference that such velocity is to some extent independent of the velocity of the source. This again is nothing stranger than what is assumed in Relativity for light. If the velocity is independent of the velocity of the source, the cross-radial momentum cannot be produced. Even if it is dependent, but only partially, there would be a net difference in the losses of momenta at the rear and in the front. (3) The assumption that the emissions are radial is the resultant average effect of the emissions from all particles in all directions. It is of course not the fact that the whole mass is really condensed at the centre with radial emissions from it; the practical result is as if the whole mass were so concentrated and the emissions were radial. From the symmetrical shape of a hemisphere, it will be apparent that the emissions from all corresponding points normal to its motion would balance one another, while their components along that direction will combine. (4) Radiation from the Sun alone means a loss of 250 million tons of mass per minute. Light is also known to exert pressure like moving material particles. And though it behaves like material particles, its velocity is not yet known to depend on the velocity of its source. (5) It was shown in Chapter IV that the existence of gravitons is not at all necessary, and the ordinary light corpuscles are quite sufficient to explain the motion of the nebulæ.

2. (1) According to Newton's law of the conservation of momentum only when m and v are both constant,

$$\frac{d(m.v)}{dt} = m\frac{dv}{dt} + v\frac{dm}{dt} = 0 + 0 = 0.$$

But if the mass were somehow being annihilated, then if

$$\frac{d(m.v)}{dt} = 0, \text{ we shall have } \frac{dv}{dt} = -\frac{v}{m}\frac{dm}{dt} \neq 0,$$

i.e., a net acceleration when the mass is decreasing.

(2) In the new theory, de Sitter's test of the binary stars is taken as proof of the observed fact that the velocity of the light emitted from a moving star whether from the front or the back is nearly the same. It is then shown that if light consisted of swarms of material radions, the effect on the star would be an acceleration in the direction of motion.

If a system consisting of a big mass M and two tiny masses m at the front and in the rear were moving with velocity v, then its momentum will be $mv+Mv+mv$. Now if owing to internal action and reaction the tiny masses were thrown forward and backward with velocity c in space and M be moving with v', the momentum of the system will be $-mc+Mv'+mc$. Hence $v'=\left(1+\frac{2m}{M}\right)v$, *i.e.*, there is necessarily an increase in the velocity of the remaining body M in the direction of its motion.

The new theory merely explains that when a body is moving and at the same time losing mass equally in all directions owing to internal action and reaction, then if it is stationary the losses would balance each other; but if the body be moving while losing mass, there would be less momentum lost in the front than at the rear, yielding a net acceleration.

(3) Except in the extreme case when light particles emerging from a nebula have velocity $c+v$ in the front and $c-v$ at the back, there must always be a difference in the losses of momenta causing a continual change in velocity. All that is necessary for the theory is that the velocity of emerging light in space should be $< c+v$ in front and $> c-v$ at the rear.

Section V

SUNDRY POINTS

1. An eminent physicist of London, whose name I cannot disclose without previous permission, suggested that the factor in (4·3) on p. 7 of my theory might be $(1-v/D)^4$. The Appendix to Chapter I (pp. 259-60) was added in deference to this suggestion in order to elaborate the point.

2. Another critic doubted whether equation (24·9) on page 261 was right. The Doppler principle undoubtedly gives the frequency $\dfrac{1-\frac{v'}{D}}{1-\frac{u}{D}}$ (see Chapter VII, Sec. II (1). As regards the relative distance, obviously the single journey method determines the gravitational effect. For a continued length of time the effect is practically the same as if A were at rest and B were moving away from it with velocity $(v'-u)$. Hence the result is nearly the same as in (24·14).

3. The factor $\left(1-\frac{v}{\mathrm{D}}\right)^3$ has been obtained on the assumption that there is an expansion similar to that of spherical waves propagated with a finite velocity D outwards equally in all directions. A modified physical theory can certainly yield a different power and can also produce a similar factor in the denominator. It will therefore be convenient to have a generalised form from which the exact power can afterwards be deduced by equating it to the observed value.

4. Let us assume as a generalised form $(1-v/\mathrm{D})^m \,.\, (1+v/\mathrm{D})^n$. (25·1) where m and n are any integers, positive or negative. The factor then is $=\left(1-\frac{m-n}{\mathrm{D}}\cdot\, v\right)$ nearly, where v/D is small. This will mean a substitution of $(m-n)$ for 3 in (5·41) and (5·61) on p. 9; and $(m-n)$ for 3 and $(m-n-1)$ for 2 in (5·8) and (5·9) on p. 10.

For a nearly circular orbit the formula (11·13) for the advance of perihelion would then become

$$\epsilon=\frac{m-n}{\mathrm{D}^2}\cdot\frac{\mu^2}{h^2}\cdot\frac{\theta}{(1+k\theta)^2}\cdot \qquad (25\cdot2)$$

Similarly, in (14·4) on p. 26, (assuming that it holds for light) the equation for the deflection of light, $(m-n)$, will be substituted for 3 and

$$\text{then } \frac{d^2u}{d\theta^2}+u=\frac{(m-n+1)}{c^2}\cdot\, u^2 \qquad (25\cdot3)$$

Hence the deflection will be $\frac{2(m-n+1)}{3}$ times Newton's value.

Thus the effect of these changes will make no difference in the concordance with observation if

$$\frac{m-n}{\mathrm{D}^2}=\frac{3}{c^2},\ i.e.,\ \mathrm{D}=\sqrt{\frac{m-n}{3}}\cdot\, c.$$

As a particular case, if $(m-n)=2$ the rate of the advance of the perihelion would be reduced to two-thirds; while the minimum deflection of light would be equal to that in Einstein's Relativity.

5. One learned critic wondered whether my formulæ give values tallying with observation, and wanted a proof that $\mathrm{D}=c$, nearly.

$$\text{From (11·13) } \epsilon=\frac{6\pi\mu^2}{\mathrm{D}^2h^2\,(1+2\pi k)^2}=\frac{6\pi\mu^2}{c^2h^2}\ \{1+2\times 3{\cdot}1416\times 1{\cdot}628\times 10^{-4}\}$$

for Mercury if $\mathrm{D}=c$.

$$=\frac{6\pi\mu^2}{c^2h^2} \text{ nearly, just as in Relativity,}$$

tallying with Newcomb's observation.

From (14·5) and (14·6) the deflection of light comes to
$= \frac{8}{3}$ times the Newtonian value if $D = c$, nearly
$= 2''\cdot32$ tallying far more closely with observation than Einstein's value.

From (15.2) the spectral shift, if $D = c$, comes to ·00836 tallying with the Relativity value ·0084.

It is also clear that when $D = c$ satisfies three independent and different equations and makes them tally with observation, it is proved that the velocity of gravitation is nearly equal to that of light.

As against this, the position in Relativity is hopeless. With regard to the speed of the propagation of gravitation, Eddington remarks:—

"If co-ordinates are chosen so as to satisfy a certain condition which has no clear geometrical importance, the speed is that of light; if the co-ordinates are slightly different the speed is altogether different from that of light. The result stands or falls by the choice of co-ordinates." He expresses the opinion that "The speed of gravitation is quite definite; only the problem of determining it does not seem to have yet been tackled correctly." [9]

6. As to avoid confusion recourse will not in future be had to gravitons, the formula for Newton's Gravitational constant obtained on the physical theory of gravitons is here put down, but the proof is withheld:

$$F = \left(\frac{N^2 a^2 \mu D}{32t}\right)\frac{MM^1}{R^2} \quad . \quad . \quad . \quad . \quad . \quad (25\cdot4)$$

where n = the number of gravitons emitted per unit mass per unit time; N = number of gravitons emitted from a unit mass at a time; t = the time interval after which they are emitted; a = the radius of a graviton; μ = the mass of a graviton; D = the velocity of gravitons.

$$\text{Hence } G = \frac{N^2 a^2 \mu D}{32t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25\cdot5)$$

$$\text{The dimension of } G = \frac{L^3}{T^2} \cdot$$

7. I am grateful to the Editor of *Nature*[10] for an appreciative review in which after referring to my Theory he remarked "In short, an attempt is made to give an alternative explanation for the whole range of phenomena usually adduced in support of Einstein's theory" and concluded "If it can stand the test of criticism, it will obviously be of

great importance." I need hardly say that considering the variety of matters dealt with, I cannot possibly hope that the whole paper is altogether flawless. If the fundamental ideas be acceptable and the theory prove to be on right lines, and the mistakes, if any, rectifiable, my labour would be amply rewarded.

8. I must also express my thankfulness to the Editor of *Science*[11] for encouraging reviews of my Theory, characterised as "A sane border line between classical mechanics of Sir Issac Newton and the newer concepts of Prof. Einstein", which have helped to draw the attention of eminent mathematicians and scientists to it.

9. My thanks are equally due to the Editor of the *Science News Letter* for giving publicity to my theory.[12]

CHAPTER VII

Observed Relative Velocity

INTRODUCTORY

Relativity takes pride in the conception that Newton's absolute velocity is impossible of measurement, whereas relative velocity as observed is a measurable quantity. But it was pointed out in Chapter V, Section I, para 5, pp. 241-2 that Einstein's rejection of Newton's absolute velocities has not improved things in any way, but has rather made relative velocity as observed an uncertain quantity, depending on the particular method of measurement chosen, and varying as the method is changed. Relative velocity (other than the difference between Newton's absolute velocities) would then cease to have any definite meaning and merely indicate something shown by a particular experiment, different experimenters using different experiments would arrive at entirely different results. It is just as impossible to measure exactly the actual relative velocity, *i.e.*, the real difference between two absolute velocities as to measure the absolute velocities separately.

SECTION I

THE SINGLE JOURNEY METHOD

1. In Relativity it is assumed that velocity of light is absolute, and that light takes the same time to go from one moving body A to another moving body B no matter how differently the two bodies be moving. Einstein defines common time between A and B by quite arbitrarily assuming that "the time which light requires in travelling from A to B is equivalent to the time which light requires in travelling

from B to A." [13] This assumption is an utter physical impossibility when the two velocities are different, and can be true only in the case where the two bodies are moving with exactly equal velocities, either both towards each other or both away from each other. The times taken by light in single journeys are $\frac{r}{c-v}$, and $\frac{r}{c+u}$ and they cannot be equal for all values of v' and u. It is this impossible assumption which is the main foundation of Relativity.

2. The above wrong assumption involves indirectly the assumption that relative velocity between two bodies can be measured somehow by a single journey of light. Now a slight reflection would make it obvious that it is impossible to conduct an experiment by sending out a messenger from one moving body to another moving body which would determine the relative velocity. If the velocity in space of the messenger is independent of the source, then he would lose touch with the body which he has left, and will be able only to measure the distance travelled by himself by noting the time taken by himself, and nothing more. Indeed it is well known that in all the experiments for measuring the velocity, light is made to perform the double journey. "The light traverses one and the same path in its journey there and back. It is only a mean velocity during the path to and fro that is actually observed." (Max Born).[14]

3. Again, if only a single journey velocity is taken, then the result would be different according as one or the other body is taken as the source, and the other the observer.

(1) A messenger sent out from B will take $\frac{r}{c+u}$ time to reach A, and then the distance between the two bodies would be

$$A'B' = r + (v'-u)\frac{r}{c+u} = \frac{c+v'}{c+u}\,r \quad . \quad . \quad . \quad (26{\cdot}1)$$

If A imagines himself to be at rest, then the time and distance according to him would be

$$\frac{r}{c} \text{ and } r + (v'-u)\frac{r}{c} = \frac{c+v'-u}{c}\,r \quad . \quad . \quad . \quad (26{\cdot}2)$$

Hence the ratio would be

$$\frac{v}{v'-u} = \frac{(c+v'-u)\dfrac{r}{c}}{\dfrac{r}{c}} \times \frac{\dfrac{r}{c+u}}{\dfrac{c+v'}{c+u}\cdot r}$$

$$= \frac{c+v'-u}{c+v'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26{\cdot}3)$$

(2) On the other hand, a messenger sent out from A will take time $\frac{r}{c-v'}$, and the distance

$$A_1B_1 = r + (v'-u)\frac{r}{c-v'} = \frac{c-u}{c-v'}r. \quad . \quad . \quad . \quad (26{\cdot}4)$$

But if B imagines himself at rest, he gets the same values for time and distance as A, *i.e.*, $\frac{r}{c}$ and $r+(v'-u)\frac{r}{c} = \frac{c+v'-u}{c}$. . . . . (26·5)

Hence the ratio would be

$$\frac{v}{v'-u} = \frac{c+v'-u}{c-u} \quad . \quad . \quad . \quad . \quad . \quad (26{\cdot}6)$$

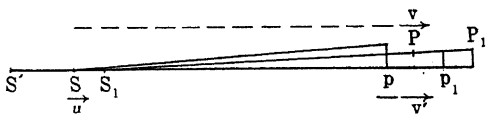
It is obvious that the values would be different in the two cases unless one wrongly assumes that $\frac{r}{c+v'} = \frac{r}{c-u}$ for all values of u and v'.

Although it has to be conceded that for a single journey the Doppler effect is different according as one body is the source or the other, Relativity astonishingly assumes that for a single journey the Relative velocity is the same.

Section II

THE METHOD OF PARALLAX

Subtended angles.



(1) Let an object of height h subtend angles α and α_1 at S and S_1, which are the positions of S at times t and t_1. Similarly, let P and P_1 be then the positions of an object P. Let the velocities of S and P be u and v' respectively with reference to S′ supposed to be at rest. Let v be the velocity of P as measured by S. The actual relative velocity of P is $(v'-u)$.

As light takes time to travel from P to S, it is obvious that the image received by S started from a nearer position p than P.

At time t, S measures the angle α subtended by the image which left p, and so $Sp = h \cot \alpha$.

But this image left p at time $\left(t - \frac{h \cot \alpha}{c}\right)$.

Again at time t_1, S_1 measures the angle α_1, which left the object from p_1 nearer than P_1.

So that $S_1\ p_1 = h \cot \alpha_1$.

But this image had left p_1 at time $\left(t_1 - \frac{h \cot \alpha_1}{c}\right)$.

Hence while an observer moving from S to S_1 measures the time interval as $= (t_1 - t) = T$

$$\text{the real lapse of time} = \left(t_1 - \frac{h \cot \alpha_1}{c}\right) - \left(t - \frac{h \cot \alpha}{c}\right)$$

$$= T - \frac{h (\cot \alpha_1 - \cot \alpha)}{c} = \left(T - \frac{\beta}{C}\right)$$

where $\beta = h (\cot \alpha_1 - \cot \alpha)$.

Now S measures the distance travelled by P as $= h\ (\cot \alpha_1 - \cot \alpha)$. Hence the velocity of P as measured by S is

$$v = \frac{h (\cot \alpha_1 - \cot \alpha)}{T} = \frac{\beta}{T}. \quad \quad (27{\cdot}1)$$

But the real distance travelled by P in the real time is

$$\begin{aligned} pp_1 &= SS_1 + S_1\ p_1 - Sp \\ &= Tu + h\ (\cot \alpha_1 - \cot \alpha) \\ &= Tu + \beta. \end{aligned}$$

Hence the real velocity of P is

$$(v' - u) = \frac{Tu + h\ (\cot \alpha_1 - \cot \alpha)}{T - \dfrac{h\ (\cot \alpha_1 - \cot \alpha)}{c}}$$

$$= \frac{Tu + \beta}{T - \dfrac{\beta}{c}}. \quad \quad (27{\cdot}2)$$

$$\therefore \quad \frac{v}{v' - u} = \frac{\beta}{T} \times \frac{\left(T - \dfrac{\beta}{c}\right)}{Tu + \beta} = \frac{\beta}{T} \times \frac{1 - \dfrac{\beta}{T} \cdot \dfrac{1}{c}}{u + \dfrac{\beta}{T}}$$

$$= \frac{k\left(1 - \dfrac{k}{c}\right)}{u + k} \quad \quad (27{\cdot}3)$$

where $k = \frac{\beta}{T}$.

(2) If $u = 0$, and $\frac{\beta}{T} \cdot \frac{1}{c}$ is small compared to the relative velocities then $v = v' - u$ (Newtonian form).

In any case, as the velocities are small compared to c, and the angles α and α_1 are nearly equal, actual observations on the earth do not show any difference from the Newtonian form. Otherwise the result would be different.

SECTION III

THE FLASH METHOD

Let S′ be at rest and S and P move with velocities u and v'.

At time t, the positions are S and P; the previous positions of P and P_1 are p and p_1. At time t_1 the positions are S_1 and P_1.

When light flashes are received by S from P, S measures the time apparently as $(t_1 - t) = T$ . . . . (28·1)

But the flash received by S and S_1 started from p and p_1. So the real time is

$$T_0 = (t'_0 - t_0) = \left(t_1 - \frac{S_1 p_1}{c}\right) - \left(t - \frac{Sp}{c}\right)$$

$$= \left(T - \frac{S_1 p_1 - Sp}{c}\right) \quad . \quad . \quad . \quad . \quad (28·2)$$

The distance travelled by P as seen by S is $l = S_1 p_1 - Sp$, because S received messages from p and p_1 at S and S_1 . . . . . . (28·3)

But the real distance travelled by P as seen by S′ is

$$l_0 = pp_1 = Sp_1 - Sp = SS_1 + S_1 p_1 - Sp \quad . \quad . \quad . \quad (28·4)$$

Now $\qquad \frac{pP}{v'} = \frac{Sp}{c}$ and $\frac{p_1 P_1}{v'} = \frac{S_1 p_1}{c}$

But $\qquad$ time $\left(t_0 + \frac{pp_1}{v'} + \frac{S_1 p_1}{c}\right) = \left(t_0 + \frac{Sp}{c} + \frac{SS_1}{u}\right)$

and $\qquad \frac{S_1 p_1}{c} - \frac{Sp}{c} = \frac{SS_1}{u} - \frac{pp_1}{v'}$

$$= \frac{SS_1}{u} - \frac{SS_1 + S_1 p_1 - Sp}{v'}.$$

Hence $$(S_1 p_1 - Sp).\left(\frac{1}{c} + \frac{1}{v'}\right) = SS_1\left(\frac{1}{u} - \frac{1}{v'}\right).$$

But $SS_1 = Tu.$

$$\therefore \quad S_1 p_1 - Sp = Tu. \left(\frac{v'-u}{v'+c}\right).\frac{c}{u}.$$

Hence $$\frac{T}{T_0} = \frac{T}{T - \dfrac{S_1 p_1 - Sp}{c}} = \frac{T}{T - T.\dfrac{v'-u}{v'+c}} \quad . \quad . \quad (28\cdot5)$$

$$\therefore \quad T_0 = T\left(1 - \frac{v'-u}{v'+c}\right) = T.\frac{c+u}{c+v'} \quad . \quad . \quad . \quad (28\cdot6)$$

And $$\frac{l}{l_0} = \frac{S_1 p_1 - Sp}{S\,S_1 + (S_1 p - Sp)} = \frac{Tu.\dfrac{v'-u}{v'+c}.\dfrac{c}{u}}{Tu + Tu.\dfrac{v'-u}{v'+c}.\dfrac{c}{u}}$$

$$= \frac{\dfrac{v'-u}{v'+c}.\dfrac{c}{u}}{1 + \dfrac{v'-u}{v'+c}.\dfrac{c}{u}} = \frac{c\,(v'-u)}{v'\,(c+u)}. \quad . \quad . \quad (28\cdot7)$$

The result would of course be different if P be the observer.

SECTION IV

THE METHOD OF WAVELENGTH OR SPECTRAL SHIFT

1. *The Doppler Effect.*

(1) Let A be the source moving with velocity u and B the observer moving with v'. Let λ and T denote the wavelength and period.

As waves come out from A, $\lambda_1 = \lambda_0 - u.\,T_0 = \lambda_0 - \frac{u}{c}.\,\lambda_0$

$$= \lambda_0\left(1 - \frac{u}{c}\right)$$

As waves reach B′, $$\lambda_2 = \lambda_1 + v'T_2 = \lambda_1 + v'\frac{\lambda_2}{c}$$

$$\lambda_1 = \lambda_2\left(1 - \frac{v'}{c}\right)$$

Hence $$\lambda_2 = \frac{\left(1-\frac{u}{c}\right).\lambda_0}{\left(1-\frac{v'}{c}\right)} \quad . \quad . \quad . \quad . \qquad (29{\cdot}1)$$

$$= \left(1+\frac{v'}{c}-\frac{u}{c}-\frac{v'u}{c^2}+\frac{v'^2}{c^2}-\frac{v'^2u}{c^3}+\frac{v'^3}{c^3}\right)\lambda_0 \quad . \quad . \quad . \qquad (29{\cdot}2)$$

This holds good whether $v' \lesseqgtr u$.

(2) Let A be the observer and B the source.

As waves emerge from B, $\lambda_1=\lambda_0+v'.\,T_0=\lambda_0+v'.\frac{\lambda_0}{c}=\left(1+\frac{v'}{c}\right).\lambda_0.$

As waves reach A′, $\lambda_2=\lambda_1-u.\,T_2=\lambda_1-u\,\frac{\lambda_2}{c}$

$$\lambda_1=\left(1+\frac{u}{c}\right).\lambda_2.$$

Hence $$\lambda_2=\frac{\left(1+\frac{v'}{c}\right)}{\left(1+\frac{u}{c}\right)}\lambda_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (29{\cdot}3)$$

$$=\left(1+\frac{v'}{c}-\frac{u}{c}-\frac{v'u}{c^2}+\frac{u^2}{c^2}+\frac{v'u^2}{c^3}-\frac{u^3}{c^3}\right)\lambda_0 \quad . \quad . \quad . \qquad (29{\cdot}4)$$

2. Now if the change in the wavelength of light were to depend exclusively on the relative velocity V of the two bodies and be independent of the absolute velocities then $\lambda+d\lambda=\left(1+\frac{V}{c}\right)\lambda$

$$\therefore \quad \frac{d\lambda}{\lambda}=\frac{V}{c}.$$

Hence if the apparent relative velocity be v and the real relative velocity $(v'-u)$, then

$$\lambda_0+d\lambda=\left(1+\frac{v}{c}\right)\lambda_0 \quad \text{and} \quad \frac{d\lambda}{\lambda_0}=\frac{v}{c}$$

while $$\lambda_0+d\lambda_0=\left(1+\frac{v'-u}{c}\right)\lambda_0 \text{ and } \frac{d\lambda_0}{\lambda_0}=\frac{v'-u}{c}.$$

According to Newton $v=v'-u$ and $\therefore\ d\lambda=d\lambda_0$.

But if $v=f.\,(v'-u)$, then $d\lambda=f.\,d\lambda_0$ . . . . (29·5)

3. Now as $V=c.\frac{d\lambda}{\lambda}$, if the wavelength depended on the relative velocity only, then

$$(v'-u)=c.\frac{d\lambda}{\lambda_0} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (29{\cdot}6)$$

Thus the spectral shift $\frac{d\lambda_0}{\lambda_0}$ will determine the apparent relative velocity deduced on the wrong assumption.

4. It is now apparent that

(a) If the wavelength be wrongly supposed to depend on the relative velocity only then the apparent relative velocity v is supposed to be equal to $v'-u$ and is taken to be $c. \frac{d\lambda}{\lambda_0}$.

(b) But if the source be moving with velocity v' and the observer with u, then the real relative velocity

$$= (v' - u) - \frac{v'u}{c} + \frac{u^2}{c} + \frac{v'u^2}{c^2} - \frac{u^3}{c^2} \quad . \quad . \quad . \quad (29{\cdot}7)$$

Hence the error in the assumption

$$= -\frac{v'u}{c} + \frac{u^2}{c} + \frac{v'u^2}{c^2} - \frac{u^3}{c^2}. \quad . \quad . \quad . \quad . \quad (29{\cdot}8)$$

(c) It is also clear that the relative velocity as measured by B would be different and would have the error

$$= -\frac{v'u}{c} + \frac{v'^2}{c} - \frac{v'^2u}{c^2} + \frac{v'^3}{c^2} \quad . \quad . \quad . \quad . \quad (29{\cdot}9)$$

It follows that the relative velocity would be different according as one or the other is the observer.

Section V

THE DOUBLE JOURNEY METHOD

1. A new method of measuring common time and distance and also the ratio of real and apparent relative velocities based on a double journey of light was given in Ch. V, Sec. II, pp. 242—45. All experiments with light measure only the average to-and-fro velocity. Hence the double journey method is the only practical method of measuring relative velocities when a messenger, like light, is employed which has a nearly constant velocity in space. Suppose that two bodies A and B are moving with uniform velocities u and v' in space. A flash of light is sent out from a source on A and falls on a reflector on B and returns to A and the time taken for the double journey is noted as t. Then a second flash is immediately sent out

and the time taken is noted as t'. Let r and $r+\delta r$ be the distances between the bodies at the time when the flashes are sent out.

From (23·1) $\quad t=\dfrac{2.D.r}{(D-v')(D+u)}$ and $t'=\dfrac{2.D(r+\delta r)}{(D-v')(D+u)}$

also $\quad \dfrac{t'}{t}=\dfrac{r+\delta r}{r} \quad \therefore \quad \dfrac{t'-t}{t}=\dfrac{\delta r}{r}.$

Now the increase of the distance between the two bodies is δr in time t, *i.e.* their real relative velocity is $(v'-u)=\dfrac{\delta r}{t}=\dfrac{\delta r}{r}\cdot\dfrac{r}{t}=\dfrac{t'-t}{t}\cdot\dfrac{(D-v')(D+u)}{2.D}$

$$=\frac{(D-v')(D+u)}{2D}\cdot\left(\frac{t'-t}{t}\right). \qquad (30·1)$$

As shown in Ch. V, Sec. II, the result is the same even if B is used as source and A as the reflector, provided the clocks at A and B keep the same absolute time.

Similarly, if A is wrongly assumed to be at rest and B moving with relative velocity $(v'-u)$ or if it be wrongly assumed with Newton that the result will be the same if A is reduced to rest by adding an equal and opposite velocity to B then from (23·5)

$$t_1=\frac{2.r'}{D-v'+u} \text{ and } t'_1=\frac{2(r+\delta r)}{D-v'+u}$$

also $\quad \dfrac{t'_1}{t_1}=\dfrac{r+\delta r}{r}$

$$\therefore \frac{t'_1-t_1}{t_1}=\frac{\delta r}{r}$$

Hence the apparent relative velocity is

$$v=\frac{\delta r}{t_1}=\frac{\delta r}{r}\cdot\frac{r}{t_1}=\frac{t'_1-t_1}{t_1}\cdot\frac{D-v'+u}{2}$$

$$=\frac{D-v'+u}{2}\cdot\frac{t'_1-t_1}{t_1} \qquad (30·2)$$

But as the observer and his clock are the same $\dfrac{t'_1-t_1}{t_1}=\dfrac{t'-t}{t}$

Hence $\quad \dfrac{v}{v'-u}=\dfrac{D-v'+u}{2}\div\dfrac{(D-v')(D+u)}{2D}$

$$=\frac{D(D-v'+u)}{(D-v')(D+u)}=\frac{1-\dfrac{v'}{D}+\dfrac{u}{D}}{\left(1-\dfrac{v'}{D}\right)\left(1+\dfrac{u}{D}\right)} \qquad (30·3)$$

Same as already found in (23·29).

2. If a third flash is sent out immediately and is then reflected back,

then $$t'' = \frac{2D.(r+\delta r+\triangle r)}{(D-v')(D+u)} \quad \text{and} \quad t''_1 = \frac{2(r+\delta r+\triangle r)}{D-v'+u}$$

It is obvious that for each such extra observation a new unknown quantity is introduced. Hence no matter how many times the observation be repeated it will ever be impossible to know exactly the absolute velocity of either of the two bodies. In the same way it will be impossible to know the exact value of r at any point of time, though the total distance travelled by the messenger in the double journey will obviously be $D.t$.

3. It will be seen that to the first order term, the formula gives Newton's value $v=v'-u$, and to the second order term, the value

$$v = \frac{v'-u}{1-\frac{v'u}{D^2}}.$$

For higher approximations, the relative value is a function of the actual values v' and u taken separately and not only of their difference $(v'-u)$. Accordingly, the value would vary slightly with v' and u. There would also be a slight variation if the method were somewhat changed as in Ch. V, pp. 247-48.

4. Similarly, the relativity formula is true only as a second approximation, but is not rigorously true. The actual value of the apparent relative velocity depends on the particular method of observation chosen, and so is an indefinite quantity.

CHAPTER VIII

Further Corrections to Newton's Law

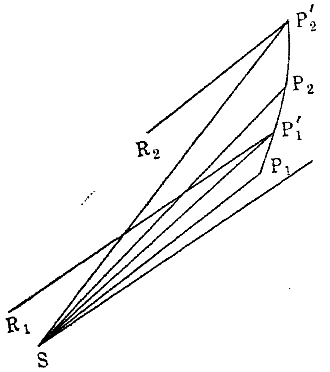
SECTION I

RETARDED GRAVITATION

I. *Of a stationary body.*

1. Newton assumed that Gravitational influence from the sun S would arrive at a planet P instantaneously, and would act in the same way no matter how fast and in which direction the planet may be moving. This meant that the velocity of gravitation must be infinite. If the velocity be finite then two corrections are necessary: (1) The influence when acting on the planet acts in a shifted direction, which has already been pointed

out in Chap. I, Secs. IV and V. (2) The influence will take time to arrive, with the result that the planet would have moved forward in the interval.



2. Newton assumed that the attractive pulls at P_1 along $P_1S = \frac{\mu}{r^2}$

at P_2 along $P_2S = \frac{\mu}{(r+dr)^2}$ etc. etc.

Really the pulls act at P'_1 along P'_1R_1 and at P'_2 along P'_2R_2, etc., where $SP'_1 = r+\delta r$ and $SP_2' = (r+dr)+\delta\,(r+dr)$, etc.

Hence the magnitudes of these pulls as shown in Appendix to Ch. I (pp. 259-60) are all decreased in the ratio $\frac{1}{\left(1+\frac{\delta r}{r}\right)^2} = \left(1-\frac{1}{D}\frac{dr}{dt}\right)^2$.

The frequency will add another factor $\left(1-\frac{1}{D}\frac{dr}{dt}\right)$. These results were taken into account in the equations previously.

3. Now the other effect will be that by the time the gravitational influence overtakes the planet, it will have moved further by a distance δr and rotated by an angle $\delta\theta$, where

$$\delta r = \frac{dr}{dt}\,\delta t = \frac{dr}{dt}\cdot\frac{r+\delta r}{D} = \frac{r}{D}\frac{dr}{dt} \text{ nearly} \quad . \quad . \quad . \quad (31\cdot1)$$

$$\text{and } \delta\theta = \frac{d\theta}{dt}\,\delta t = \frac{d\theta}{dt}\,\frac{r+\delta r}{D} = \frac{r}{D}\frac{d\theta}{dt} \text{ nearly} \quad . \quad . \quad . \quad (31\cdot2)$$

By substituting $(r+\delta r)$ for r and $(\theta+\delta\theta)$ for θ in (5·41) and neglecting $d\,(\delta t)$ for a nearly circular orbit we get in place of Newton's equation the following—

$$\frac{d}{dt}\left\{(r+\delta r)^2\frac{d}{dt}(\theta+\delta\theta)\right\} = \frac{\mu}{D}\frac{d}{dt}(\theta+\delta\theta) \quad . \quad . \quad . \quad (31\cdot3)$$

$$\text{and } \frac{d^2}{dt^2}(r+\delta r) - (r+\delta r)\left\{\frac{d}{dt}(\theta+\delta\theta)\right\}^2 = -\frac{\mu}{(r+\delta r)^2}$$
$$-\frac{(m-n)\mu}{D^2}\left\{\frac{d}{dt}(\theta+\delta\theta)\right\}^2 + \frac{(m-n)}{D}\frac{\mu}{(r+\delta r)^2}\frac{d}{dt}(r+\delta r) \quad . \quad (31\cdot4)$$

which when simplified give

$$\frac{d}{dt}\left(r^2\frac{d\theta}{dt}\right) = \frac{\mu}{D}\frac{d\theta}{dt} - \frac{2\mu}{D^2}\frac{dr}{dt}\frac{d\theta}{dt} \quad . \quad . \quad . \quad (31\cdot5)$$

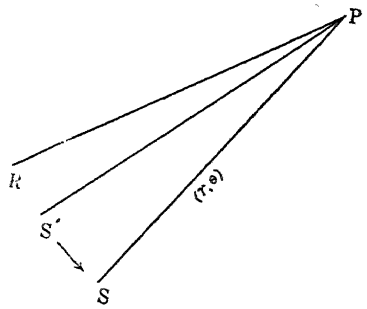
and $$\frac{d^2r}{dt^2} = -\frac{\mu}{r^2} - (m-n)\frac{\mu}{D^2}\left(\frac{d\theta}{dt}\right)^2 + (m-n+3)\frac{\mu}{D}\frac{1}{r^2}\frac{dr}{dt}$$

$$-(m-n)\frac{\mu}{D^3}\left(\frac{d\theta}{dt}\right)^2\frac{dr}{dt} - 2(m-n)\frac{\mu}{D^2}\frac{1}{r^2}\left(\frac{dr}{dt}\right)^2 \quad . \quad . \quad (31{\cdot}6)$$

The two extra terms on the right-hand side of (31·5) and the four extra terms on the right-hand side of (31·6) can be treated as transverse and radial disturbing forces superimposed on Newtonian force.

II. *Of a moving body.*

Let S and P be the present positions of the sun and the planet. Owing to the delay in the arrival of gravitation the influence arriving at P now really started from S′ and not S, and has come along S′P and acts along PR.



Hence the force coming along S′P $= -\frac{\mu}{(r-\delta r)^2}$ where as before $-\delta\theta = \frac{r}{D}\frac{d\theta}{dt}$

and $$-\delta r = \frac{r}{D}\frac{dr}{dt} \quad . \quad . \quad . \quad . \quad . \quad (31{\cdot}7)$$

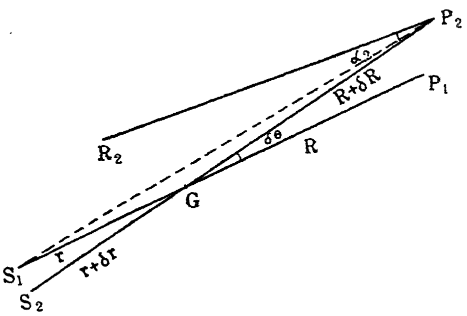
The previous method can be followed in exactly the same way.

It is also apparent that in Laplace's theory the first order terms would cancel each other, and the effect on the perturbations would be practically nil.

Section II
TWO MOVING BODIES

Geometrical method.

1. Both the sun and the planet would obviously revolve round their common centre of gravity G in opposite directions, with equal angular velocities in such a way that their distances from G and their masses have the ratios $\frac{r}{R} = \frac{GS}{GP} = \frac{m}{M}$ and so M. SP $=(M+m)$ GP.



Hence the Newtonian force of attraction of the sun on the planet is $\frac{G.M}{SP^2} = \frac{G.M}{\left(1+\frac{m}{M}\right)^2 . GP^2}$ which is equivalent to a mass $\frac{M}{\left(1+\frac{m}{M}\right)}$ acting from G.

2. Now if S_1 and P_1 be the present positions, then instead of the gravitation coming along S_1P_1 and acting at P_1 as Newton supposed, it will come along S_1P_2 and act along P_2R_2. Also $\delta R = \frac{R+r}{D} \frac{dR}{dt}$ and

$$\delta\theta = \frac{R+r}{D} \cdot \frac{d\theta}{dt} \quad \ldots \ldots \quad (32\cdot1)$$

But $d_2^2 = S_1P_2^2 = r^2 + (R+\delta R)^2 - 2r\,(R+\delta R)\cos(\pi - \delta\theta)$

$$= R^2\left(1+\frac{m}{M}\right)^2\left[1+\frac{2}{D}\frac{dR}{dt} - \frac{m}{M}R^2\left(\frac{d\theta}{dt}\right)^2 \times \left\{1+\frac{1}{D}\left(1+\frac{m}{M}\right)\frac{dR}{dt}\right\}\right] \quad . \quad (32\cdot2)$$

$$\frac{\operatorname{Sin}\beta_2}{\operatorname{Sin}(\pi-\delta\theta)} = \frac{r}{d_2}$$

$$\therefore \operatorname{Sin}\beta_2 = \frac{\operatorname{Sin}\delta\theta}{d_2} = \frac{r\delta\theta}{d_2} = \frac{r}{d_2}\,w.\delta t = \frac{rw}{D} = \frac{m}{MD}\,R\,\frac{d\theta}{dt} \quad . \quad (32\cdot3)$$

$$\operatorname{Cos}\beta_2 = \sqrt{1-\frac{m^2}{M^2}\frac{w^2}{D^2}R^2} = 1-\tfrac{1}{2}\frac{m^2}{M^2}\frac{R^2}{D^2}\left(\frac{d\theta}{dt}\right)^2$$

where β_2 = angle $S_1P_2R_2$ . . . . (32·4)

$$\text{Also } \operatorname{Sin}\alpha_2 = \frac{Rw}{D\sqrt{1+\frac{R^2w^2}{D^2}}} \cdot \operatorname{Cos}\beta_2 = \frac{R}{D}\frac{d\theta}{dt}\left\{1-\tfrac{1}{2}\frac{R^2}{D^2}\left(\frac{d\theta}{dt}\right)^2\right\} \quad (32\cdot5)$$

$$\operatorname{Cos}\alpha_2 = 1-\tfrac{1}{2}\frac{R^2}{D^2}\left(\frac{d\theta}{dt}\right)^2 \text{ nearly.} \quad \ldots \ldots \quad (32\cdot6)$$

Hence if α be the total shift then

$\operatorname{Sin}\alpha = \operatorname{Sin}(\alpha_2+\beta_2)$

$$= \frac{R}{D}\frac{d\theta}{dt}\left\{1-\tfrac{1}{2}\frac{R^2}{D^2}\left(\frac{d\theta}{dt}\right)^2\right\}\left\{1-\tfrac{1}{2}\frac{m^2}{M^2}\frac{R^2}{D^2}\left(\frac{d\theta}{dt}\right)^2 + \frac{m}{MD}R\frac{d\theta}{dt}\right\} \quad (32\cdot7)$$

$$\operatorname{Cos}\alpha = 1-\tfrac{1}{2}\frac{R^2}{D^2}\left(\frac{d\theta}{dt}\right)^2 \text{ nearly} \quad \ldots \ldots \quad (32\cdot8)$$

It is obvious that β_2 is very small as compared to α_2.

Also $\delta\theta$ is nearly $\left(1+\frac{m}{M}\right)$ times α. So that $P_2 R_2$ is nearly parallel to S_1P_1. Thus the components along and normal to SP remain nearly the same; only an extra couple due to the displaced position comes into existence.

3. Now the distance between P_2R_2 and P_1S_1 is $R\ \delta\theta$ nearly $=\frac{R^2}{D}\frac{d\theta}{dt}\left(1+\frac{m}{M}\right)$. Hence the moment of the force whose magnitude has been shown to be practically the same as that of Newton

$$=-\frac{\mu}{(R+r)^2}\cdot R.\ \delta\theta. = \frac{\mu}{R^2\left(1+\frac{m}{M}\right)^2}\cdot\frac{R^2}{D}\cdot\frac{d\theta}{dt}\left(1+\frac{m}{M}\right)=\frac{\mu}{D}\frac{d\theta}{dt}\left(1-\frac{m}{M}\right)$$

$$\text{Hence}\ \frac{d}{dt}\left(r^2\frac{d\theta}{dt}\right)=\frac{\mu}{D}\frac{d\theta}{dt}\left(1-\frac{m}{M}\right) \qquad (32\cdot9)$$

4. *Analytical method.*—The more approximate equations of motion can be better obtained analytically. It will be convenient to refer the motion to the centre of gravity as the fixed origin. Let the coordinates of S be (r, θ) and those of P be (R, Θ). Owing to the delay in the arrival of the gravitational influence, the planet is overtaken at P_2 (*i.e.*, $R+\delta R$ $\Theta+\delta\Theta$) instead of at P_1 (R, Θ), at time $t+\delta t$ instead of time t.

$$\text{Now}\ \delta R = \frac{R+r}{D}\ \frac{dR}{dt}=\left(1+\frac{m}{M}\right)\frac{R}{D}\ \frac{dR}{dt}$$

$$\delta\theta = \frac{R+r}{D}\ \frac{d\theta}{dt} = \left(1+\frac{m}{M}\right)\frac{R}{D}\ \frac{d\theta}{dt}$$

$$\frac{d}{d(t+\delta t)}=\frac{1}{\frac{d(t+\delta t)}{dt}}\ \frac{d}{dt}=\frac{1}{\frac{d\left(t+\frac{R+r}{D}\right)}{dt}}\ \frac{d}{dt}$$

$$=\frac{1}{1+\frac{1}{D}\left(1+\frac{m}{M}\right)\frac{dR}{dt}}\ \frac{d}{dt}\cdot \qquad (32\cdot10)$$

From equations in (5·41) and (5·7), we get the following equations of motion at $(R+\delta R)$, $(\Theta+\delta\Theta)$ at time $t+\delta t$.

$$\frac{d}{d(t+\delta t)}\left\{(R+\delta R)^2\frac{d(\theta+\delta\theta)}{d(t+\delta t)}\right\}=\frac{\mu}{D}\cdot\frac{d(\theta+\delta\theta)}{d(t+\delta t)}\cdot \qquad (32\cdot11)$$

and $$\frac{d^2(R+\delta R)}{d(t+\delta t)^2} - (R+\delta R)\left\{\frac{d(\theta+\delta\theta)}{d(t+\delta t)}\right\}^2 = -\frac{\mu}{(R+\delta R)^2}$$

$$-\frac{(m-n)\,\mu}{D^2}\left\{\frac{d(\theta+\delta\theta)}{d(t+\delta t)}\right\}^2 + \frac{(m-n)\mu}{D}\,\frac{1}{(R+\delta R)^2}\,\frac{d(R+\delta R)}{d(t+\delta t)}. \quad (32\cdot11)$$

which when simplified give

$$\frac{d}{dt}\left(R^2\frac{d\theta}{dt}\right) = \left\{\frac{\mu}{D}\,\frac{d\theta}{dt} - 2R^2\frac{d\theta}{dt}\,\frac{1}{D}\left(1+\frac{m}{M}\right)\frac{d^2R}{dt^2}\right\}$$

$$\times\left\{1-\frac{1}{D}\left(1+\frac{m}{M}\right)\frac{dR}{dt}\right\} \quad . \quad . \quad . \quad . \quad . \quad (32\cdot12)$$

and $$\frac{d^2R}{dt^2} - R\left(\frac{d\theta}{dt}\right)^2 = -\frac{\mu}{R^2} - \frac{(m-n)\mu}{D^2}\left(\frac{d\theta}{dt}\right)^2 + \frac{(m-n)\mu}{D}\,\frac{1}{R^2}\,\frac{dR}{dt}$$

$$+\frac{2\mu}{DR^2}\left(1+\frac{m}{M}\right)\frac{dR}{dt} - \frac{2(m-n)\mu}{D^2R^2}\left(\frac{dR}{dt}\right)^2\left(1+\frac{m}{M}\right)$$

$$+\frac{R}{D}\left(1+\frac{m}{M}\right)\frac{dR}{dt}\left(\frac{d\theta}{dt}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad (32\cdot13)$$

The second method.—If S (r, θ) and P (R, Θ) be the present positions of the sun and the planet then their previous positions would be S′ $(r-\delta r, \theta-\delta\theta)$ and P′ $(R-\delta R, \Theta-\delta\Theta)$ at time $t-\delta t$, from which the gravitation reaches the planet now.

Then the equations of motion can be found in the same way as before by substituting $R-\delta R$ for R, $\Theta-\delta\Theta$ for Θ, and $t-\delta t$ for t.

SECTION III

REAL AND RELATIVE ORBITS

1. As the law of force is very nearly the inverse square of the distance from the common centre of gravity, it is obvious that both the sun and the planet will describe nearly elliptic orbits round the centre of gravity as focus; and each will also describe a larger ellipse relatively to the other with equal angular velocities. The major axis will depend on the magnitude of the velocity v at a distance R from G and will be given by $a = \frac{\mu' R}{2\mu' - Rv^2}$ and will be independent of the direction of the velocity

at that point; while the minor axis will depend on the angle of projection β at R and will be given by

$$b = \frac{R^{3/2}}{\sqrt{2\mu^1 - Rv^2}} \cdot v \sin \beta, \text{ where } \mu^1 = \frac{G.\ M^3}{(M+m)^2}.$$

The tangential velocities of the two bodies will be in parallel and opposite directions, the bodies being on the opposite sides of G. The orbits will remain ellipses so long as $v^2 < \dfrac{2\,G.M}{\left(1+\dfrac{m}{M}\right)^2} \; \dfrac{1}{R}$.

The orbit will be a circle if $\beta = \frac{\pi}{2}$, and the value of $b = a$.

2. Now as $\frac{m}{M} = \frac{r}{R}$ and $\theta = \Theta + \pi$ it follows that

if the sun describes the ellipse $\frac{1}{r} = \frac{\mu^1}{h^2}(1 + e\cos\theta)$ . . . . (33·1)

then the planet will describe the ellipse $\frac{1}{R} = \frac{m}{M}\,\frac{\mu^1}{h^2}(1 - e\cos\theta)$. (33·2)

and both the sun and the planet will describe relatively round each other the ellipse $\frac{1}{\rho} = \frac{1}{(R+r)} = \frac{m}{M+m}\,\frac{\mu^1}{h^2}(1 + e\cos\theta)$ . . . . . (33·3)

3. More generally, if the law of attraction be $\frac{G.M.m}{(R+r)^2}$, then the force will be $\dfrac{G.\ M.\ m}{R^2\left(1+\dfrac{m}{M}\right)}$ . . . . (33·4)

If the path of the planet round the centre of gravity be $R = F(\theta)$ the path of P relative to S will obviously be

$$\rho = (R+r) = \left(1 + \frac{m}{M}\right) F(\theta) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (33·5)$$

4. If the orbits be nearly circular then approximately R and r are constants and $\frac{dR}{dt}$ and $\frac{dr}{dt}$ are both negligible, and $\frac{d\theta}{dt} = w$ a constant. It is also clear that each planet will have the same angular velocity round the other as both have round the centre of gravity. It is also clear that the radial velocity v is zero and the transverse velocities are constants Rw and rw.

Accordingly the equations of motion are

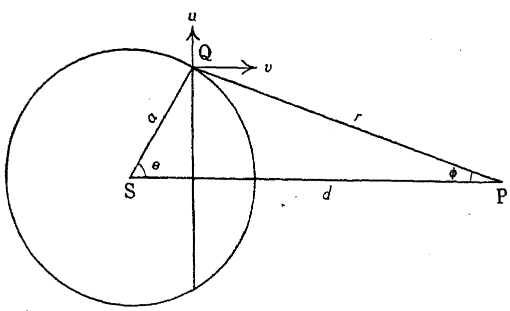
$$\frac{d}{dt}\left(R^2 \frac{d\theta}{dt}\right)=\frac{\mu}{D}\frac{d\theta}{dt}=\frac{\mu}{D}w. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (33{\cdot}6)$$

and $-R\left(\frac{d\theta}{dt}\right)^2=-\frac{\mu}{r^2}-\frac{3\mu}{D^2}\left(\frac{d\theta}{dt}\right)^2$, *i.e.*, $+Rw^2=+\frac{\mu}{r^2}+\frac{3\mu}{D^2}w^2$. . (33·7)

SECTION IV

LONGITUDINAL, TRANSVERSE AND ROTATIONAL MASSES

1. Newton assumed that the attraction of a spherical shell on a point is as if the whole mass were concentrated at the centre, whether the body is moving or is stationary. Really for a moving body a slightly different mass is concentrated at the centre. Let a spherical shell with centre S have the radius a and surface density σ; and let a point Q on the surface be such that the angle QSP $=\theta$ and QPS $=\phi$, where P is the attracted point at a distance d from S. Then the force exerted along SP by a thin annulus at Q is $f=\frac{\sigma 2\pi\ a \sin\theta.\ ad\theta}{r^2}\cos\phi$.



But $r^2=a^2+d^2-2ad\cos\theta$. $\therefore\ rdr=ad\sin\theta\, d\theta$.

Let v be the velocity of S towards P. Then the component velocity of Q along QP$=v\cos\phi$. Hence the factor due to the Doppler and aberration effects $=\left(1+\frac{v\cos\phi}{D}\right)^{m-n}$

The components perpendicular to SP cancel each other; and so do the moments caused on P by the transverse components at corresponding points.

Accordingly the total force along SP is

$$F_1=-\int\frac{\sigma\ 2\ \pi a^2\sin\theta d\theta}{r^2}.\quad \cos\phi\left(1+\frac{v}{D}\cos\phi\right)^{m-n}$$

$$=-\frac{\sigma\pi a}{d^2}\int\frac{r^2+(d^2-a^2)}{r^2}\left\{1+(m-n)\frac{v}{D}.\frac{r^2+(d^2-a^2)}{2rd}\right\}dr, \text{ nearly.}$$

$$= -\frac{\sigma\pi a^2}{d^2}\int \left\{ \left(1+\frac{d^2-a^2}{r^2}\right) + (m-n)\,\frac{vr}{2\mathrm{D}d} \right\} dr, \quad \text{nearly}$$

$$= -\frac{\sigma 4\pi a^2}{d^2}\left[1+\frac{(m-n)}{4}\frac{v}{\mathrm{D}}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34{\cdot}1)$$

Thus it slightly differs from Newton's value $\frac{\sigma 4\,\pi a^2}{d^2}$. It follows that although the mass of the moving body is not changed, its effective attraction is increased as if the mass were increased. This can be wrongly supposed to be an increased *longitudinal* mass.

2. If u be the velocity of the spherical shell at right angles to SP then similarly the velocities of Q and Q′ along PQ and PQ′ are $\pm\, u \sin\phi$. Hence the total force of attraction along SP

$$= -\int \frac{\sigma\, 2\pi\, a^2 \sin\theta\, d\theta}{r^2}\cos\phi \left\{ \left(1-\frac{u}{\mathrm{D}}\sin\phi\right)^{m-n} + \left(1+\frac{u}{\mathrm{D}}\sin\phi\right)^{m-n} \right\}$$

$= -\ \frac{\sigma\, 4\pi\, a^2}{d^2}$, the same as under Newton's Law if $\frac{u^2}{\mathrm{D}^2}$ be neglected and ϕ be small . . . . (34·2)

The components perpendicular to SP will in addition give

$$-\int \frac{\sigma\, 2\pi a^2 \sin\theta\, d\theta}{r^2}\sin\phi\left(\frac{2(m-n)}{\mathrm{D}}\sin\phi\right) \quad . \quad . \quad . \quad (34{\cdot}3)$$

which will obviously be small if d is large and therefore ϕ is small. This can be wrongly supposed to be a changed *transverse* mass.

3. Suppose the spherical shell is merely rotating with angular velocity w, parallel to the plane containing SP, then the points Q and Q′ have velocities aw with components $\pm\, aw \sin\theta$ parallel to SP and $+aw\cos\theta$ perpendicular to SP. The velocity $aw\cos\theta$ is similar to u in §2 with similar results. But the components parallel to SP being equal and opposite will almost cancel each other so far as the translational force is concerned. The attraction of Q being less than that of Q′, there would be a net backward attraction at P normal to SP. Corresponding discs above and below the plane of the paper will produce similar results, their effect normal to the plane of the paper being balanced. This can be wrongly supposed to be a changed *rotational* mass.

4. If P be a body of finite dimensions instead of a particle, then at each point the net backward attraction would be:—

$$-\frac{\mu}{r^2}\left[\left\{1-\frac{aw\sin(\theta+\phi)}{\mathrm{D}}\right\}^{m-n}\sin\phi - \left\{1+\frac{aw\sin(\theta+\phi)}{\mathrm{D}}\right\}\sin\phi\right]$$

$$= -\ \mu\left[-\ \frac{(m-n)\,aw\sin(\theta+\phi)}{\mathrm{D}}\right]\sin\phi \quad . \quad . \quad . \quad . \quad . \quad (34{\cdot}4)$$

Hence points of P which are nearer to S will have greater backward attraction than those more distant. Hence the body P in addition to the backward translational motion will experience an angular motion in the same sense as the rotation of S.

5. The more complicated problem when both the bodies are moving and are of comparable dimensions is postponed to a later chapter.

SECTION V

THE MOTION OF THE SOLAR SYSTEM

As is well known the solar system as a whole is moving through space, say with velocity ω. The velocity of gravitation in free space being constant (which is like the assumption for light in Relativity), another correction is necessary. If β be the angle which the major axis of the orbit of a planet makes with the direction of the translational motion of the solar system, then $\theta+\beta$ is the angle which the radius vector makes with that direction.

Hence the velocity along the radius vector is $\frac{dr}{dt}+\omega.\cos(\theta+\beta)$

and that along the transversal is $\frac{rd\theta}{dt}-\omega.\sin(\theta+\beta)$.

Therefore the equation of motion would become

$$\frac{d}{dt}\left(r^2\frac{d\theta}{dt}\right)=\frac{\mu}{D}.\frac{d\theta}{dt} \text{ nearly} \quad . \quad . \quad . \quad . \quad (35\cdot1)$$

$$\text{and } \frac{d^2r}{dt^2}-r\left(\frac{d\theta}{dt}\right)^2=-\frac{\mu}{r^2}\left[1-\frac{1}{D}\left\{\frac{dr}{dt}-\frac{1}{D}\left(r\frac{d\theta}{dt}\right)^2+\right.\right.$$

$$\left.\left.\omega\left(\cos\overline{\theta+\beta}+\frac{1}{D}\frac{rd\theta}{dt}\sin\overline{\theta+\beta}\right)\right\}\right]^{m-n}$$

$$=-\frac{\mu}{r^2}-\frac{(m-n)}{D^2}.\frac{h^2(1+k\theta)^2}{r^4}$$

$$+\frac{(m-n)}{D}.\frac{1}{r^2}\left[\frac{dr}{dt}+\omega\left\{\cos\overline{\theta+\beta}+\frac{h(1+k\theta)}{D}.\frac{1}{r}\sin\overline{\theta+\beta}\right\}\right] \quad . \quad (35\cdot2)$$

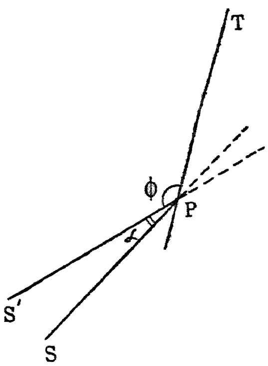
SECTION VI

ELONGATED ORBITS OF COMETS

1. The equations in Ch. I, Sec. V, pp. 8—10, were true for a heavenly body moving in a nearly circular orbit for which $\frac{v'}{D}$ was small so that $\sin\alpha = \frac{1}{D}\frac{rd\theta}{dt}$ and $\cos\alpha = 1$. The magnitude of the force also was taken to be nearly the same along the effective direction. For a comet although the tangential velocity v' as compared to D is still small, the orbit is not at all circular. For such an orbit, as shown in Ch. V, Sec. IV, p. 250, the relations are

$$\frac{\sin\alpha}{v'} = \frac{\sin(\phi-\alpha)}{D} = \frac{\sin(\pi-\phi)}{\sqrt{D^2+2v'D\cos\phi+v'^2}}$$

where ϕ is the angle between the radius vector and the tangent. Obviously



$$\frac{dr}{dt} = v'\cos(\pi-\phi) = -v'\cos\phi$$

and $$\frac{rd\theta}{dt} = v'\sin(\pi-\phi) = v'\sin\phi$$

Accordingly $$\sin\alpha = \frac{\frac{rd\theta}{dt}}{\sqrt{D^2+\left(\frac{dr}{dt}\right)^2+\left(r\frac{d\theta}{dt}\right)^2-2D\frac{dr}{dt}}}$$

$$= \frac{1}{D}\frac{rd\theta}{dt}\left(1+\frac{1}{D}\frac{dr}{dt}\right) \text{ roughly} \quad . \quad . \quad . \quad (36{\cdot}1)$$

and $$\cos\alpha = 1 - \frac{1}{2}\frac{r^2}{D^2}\left(\frac{d\theta}{dt}\right)^2 - \frac{1}{D^2}\left(\frac{dr}{dt}\right)^2 = 1 \text{ roughly} \quad . \quad (36{\cdot}2)$$

2. On the assumption, as before, that the magnitude remains nearly the same, the equations of motion become

$$\frac{1}{r}\frac{d}{dt}\left(r^2\frac{d\theta}{dt}\right) = \frac{\mu}{r^2}\left[1+\frac{v'}{D}\cos(\phi-\alpha)\right]^{m-n} \cdot \frac{v'}{D}\sin(\phi-\alpha)$$

$$= \frac{1}{r}\cdot\frac{\mu}{D}\cdot\frac{d\theta}{dt} \text{ only roughly.}$$

and $$\frac{d^2r}{dt^2}-r\left(\frac{d\theta}{dt}\right)^2=-\frac{\mu}{r^2}\left[1+\frac{v}{\mathrm{D}}\cos(\phi-\alpha)\right]^{m-n} \quad \text{nearly}$$

$$=-\frac{\mu}{r^2}\left[1+\frac{(m-n)}{\mathrm{D}^2}\left(r\frac{d\theta}{dt}\right)^2-\frac{(m-n)}{\mathrm{D}}\cdot\frac{dr}{dt}\right]$$

only very roughly.

The rough approximations can be true for nearly circular orbits only.

SECTION VII
LIGHT RADIONS

1. It was shown in Ch. II, Sec. II, pp. 25-26, that on the assumption that the equation

$$\frac{d^2u}{d\theta^2}+u=\frac{\mu}{h^2}+\frac{3\mu}{\mathrm{D}^2}\cdot u^2$$

would to a fairly close approximation hold for light, the maximum value of $h=r.\,c$, and therefore the maximum value of the deflection of light would be $\frac{8}{9}$ times that of Newton's $=2''\!\cdot\!32$ nearly, if $\mathrm{D}=c$.

2. Now on the same assumption the maximum value of the deflection of light can be easily calculated.

Following the method of Ch. I, Sec. VIII, pp. 12—13, and taking R as the shortest distance from the Sun, the first solution is $u=\frac{\cos\theta}{\mathrm{R}}$.

And therefore $$\frac{d^2u}{d\theta^2}+u=\frac{\mu}{h^2}+\frac{3\mu}{c^2\mathrm{R}^2}\cdot\cos^2\theta.$$

It will be seen that $u_1=\frac{\mu}{h^2}+\frac{\mu}{c^2\mathrm{R}^2}(\cos^2\theta+2\sin^2\theta)$ is a particular integral.

So that $$u=\frac{\mu}{h^2}+\frac{\cos\theta}{\mathrm{R}}+\frac{\mu}{c^2\mathrm{R}^2}(\cos^2\theta+2\sin^2\theta)$$

i.e., $$\mathrm{R}=\frac{\mu}{h^2}\mathrm{R}.r+r\cos\theta+\frac{\mu}{c^2\mathrm{R}}(r\cos^2\theta+2r\sin^2\theta)$$

$$=\frac{\mu}{h^2}\mathrm{R}\sqrt{x^2+y^2}+x+\frac{\mu}{c^2\mathrm{R}}\cdot\frac{(x^2+2y^2)}{\sqrt{x^2+y^2}}$$

$$\therefore\quad x=\mathrm{R}-\frac{\mu}{h^2}\mathrm{R}\sqrt{x^2+y^2}-\frac{\mu}{c^2\mathrm{R}}\cdot\frac{(x^2+2y^2)}{\sqrt{x^2+y^2}}$$

The asymptotes are found by taking y very large compared with x,

then $$x=\mathrm{R}-\frac{\mu}{h^2}.\ \mathrm{R}(\pm y)-\frac{\mu}{c^2\mathrm{R}}(\pm 2y)$$

Obviously the minimum value of $h=c.\mathrm{R}$. Hence the maximum deflection of light given by the angle between the two asymptotes $=\frac{6\mu}{c^2\mathrm{R}}$, *i.e.*, three times the Newtonian value $=2''\cdot61$ nearly.

Thus on this method the real value may, speaking roughly, be somewhere round about $2''\cdot46$.

3. (1) For radions $1=\frac{c}{\mathrm{D}}=\frac{\sin\alpha}{\sin(\phi-\alpha)}$, and so $\alpha=\frac{\phi}{2}$.

Also $-c\cos\phi=\frac{dr}{dt}$, and $c\sin\phi=r\frac{d\theta}{dt}$.

The apparent velocity of gravitation along the shifted direction $=\sqrt{\mathrm{D}^2+c^2-2\mathrm{D}c\cos(\pi-\phi)}=\mathrm{D}.2\cos\frac{\phi}{2}$.

(2) On the assumption that the method of Ch. I nearly holds good for light also, the equations of motion become

$$\frac{1}{r}\frac{d}{dt}\left(r^2\frac{d\theta}{dt}\right)=\frac{\mu}{r^2}\left[1+\left\{\cos\phi\cos\frac{\phi}{2}+\sin\phi\sin\frac{\phi}{2}\right\}\right]^{m-n}\sin\frac{\phi}{2}$$

$$=\frac{\mu}{r^2}\left(1+\cos\frac{\phi}{2}\right)^{m-n}\sin\frac{\phi}{2}. \qquad (37\cdot1)$$

and $$\frac{d^2r}{dt^2}-r\left(\frac{d\theta}{dt}\right)^2=-\frac{\mu}{r^2}\left[1+\cos\frac{\phi}{2}\right]^{m-n}\cdot\cos\frac{\phi}{2} \qquad (37\cdot2)$$

(3) If ε be the small angle between the directrix and the tangent, then $\phi=\theta+\varepsilon$.

$$\frac{1}{r}\frac{d}{dt}\left(r^2\frac{d\theta}{dt}\right)=\frac{\mu}{r^2}\left(1+\cos\frac{\theta}{2}-\frac{\varepsilon}{2}\sin\frac{\theta}{2}\right)^{m-n}\times\left(\sin\frac{\theta}{2}+\frac{\varepsilon}{2}\cos\frac{\theta}{2}\right)$$

and $$\frac{d^2r}{dt^2}-r\left(\frac{d\theta}{dt}\right)^2=-\frac{\mu}{r^2}\left(1+\cos\frac{\theta}{2}-\frac{\varepsilon}{2}\sin\frac{\theta}{2}\right)^{m-n}\left(\cos\frac{\theta}{2}-\frac{\varepsilon}{2}\cdot\sin\frac{\theta}{2}\right).$$

(4) As when light is receding from a body and gravitation cannot overtake it, the Doppler effect is not produced in the ordinary way, an additional correction will be introduced in a later chapter.

4. On the assumption that the Doppler principle and the Aberration principle are effective so long as light is approaching the sun, but cease to be effective when light begins to recede, and therefore gravitation cannot overtake it, the value of the deflection of light from a star past the sun and reaching the earth can be reduced nearly to

$$\varepsilon = -\frac{\mu}{c^2 R}\left[\int_0^{\frac{\pi}{2}}\left(1+\cos\frac{\phi}{2}\right)^3 \sin\frac{\phi}{2}\,d\phi + \int_{\frac{\pi}{2}}^{\pi} \sin\phi\,d\phi\right]$$

$$= -4{\cdot}76.\ \frac{\mu}{c^2 R} \text{ nearly}$$

i.e., $2{\cdot}39$ times the Newtonian value

$= 2''{\cdot}08$ nearly.

5. The dynamics of a changing force moving with a finite velocity and acting on a moving body is complex. Care has to be taken in compounding them, because the force causes acceleration which is of course a quantity of a different dimension from velocity. If the force were uniform or were propagated like plane waves, the simple Doppler principle would apply. But if the force is propagated like spherical waves diminishing with the distance, then a new factor appears as shown in the Appendix to Ch. I, pp. 259-60. And if the body were moving not only radially, but also possess a transverse velocity, the principle of aberration has also to be applied. Whether the magnitude of the effective force along the resultant is not changed as well will also have to be considered. In a later chapter, the problem will be re-examined from a slightly different standpoint, and the equations of motion themselves reconsidered.

CHAPTER IX

The Resisting Medium

SECTION I

THE GENERAL CASE

1. There is a growing evidence that interstellar space is filled with rarefied matter, and there is greater evidence that there are clouds of matter within the Solar System through which planets pass. The reason why in the last century a resisting medium was not accepted was that it did not

seem to have any apparent effect on the motion of planets. But the existence of Gegenschein, the shortening of the period of Enke's comet, calcium absorption and the space reddening of light are now recognised as the result of such a medium. It is far more unreasonable to suppose that space is a complete void than that some thin matter is floating about in it.

Now the resisting medium must be composed of two parts superimposed on each other (1) the interstellar matter and (2) the solar matter. The density of the former would obviously be independent of the distance of the planet from the sun, while that due to the latter would be proportional to the density, some function of r say $\rho=\psi(r)$. It is natural to suppose that the resistance due to the solar medium would decrease and not increase with the distance. It is equally clear that the acceleration R denoting the force of resistance would increase with the velocity of the planet and would be some function $F(v)$ of the velocity. It must also be proportional to the section πa^2 of the planet. The acceleration would also be inversely proportional to the mass m of the planet. Again the shape of the orbit may as well have some effect and the constant may be some function $f(a, e, w)=K$ different for different planets.

Thus the generalised form of the acceleration due to a resisting medium can be put down as

$$R=-f(a, e, w).\ F(v).\ \psi(r)\ \frac{\pi a^2}{m}$$

where $f(a, e, w)$ would approximately be constant for each orbit, particularly in major planets whose orbits are nearly circular;

$F(v)=A_0+A_1v+A_2v^2+A_3v^3+\ \ldots\ldots$
where A's are constants

and $\psi(r)=B_0+\frac{B_1}{r}+\frac{B_2}{r^2}+\frac{B_3}{r^3}+\ \ldots\ldots$

where B's are constants.

But if the solar medium is concentrated in the form of concentric shells as is quite natural, it would not be a simple function.

The General Case of Resisting Medium has been treated at length by F. Tisserand.[14]

Let $R=K.\ F(v)\ \psi.\ (r)$

where $\rho=\psi(r)$ and $K=c.\frac{\pi a^2}{m}$.

Then $$R=-K.\sum\left(A_nv^n\right).\ \sum\left(\frac{B_m}{r^m}\right) \qquad \ldots\ldots \quad (38\cdot1)$$

2. As shown in Besant's Dynamics[15], for a small tangential force, we have from $v^2 = \frac{2\mu}{r} - \frac{\mu}{a} = \frac{\mu(2a-r)}{r.a}$

$$2\, vdv = + \frac{\mu}{a^2}\, da.$$

$$\therefore \frac{da}{dt} = \frac{2a^2 v}{\mu} \cdot \text{R, where the acceleration } \text{R} = \frac{dv}{dt} \quad \ldots \quad (38\cdot2)$$

$$\text{Also } \frac{dw}{dt} = \frac{2\, r.va.\text{R} \sin\theta}{\mu e(2a-r)} \quad \ldots \quad (38\cdot3)$$

$$\text{and } \frac{de}{dt} = 2.\ \text{R}.\ (\cos\theta + e)\sqrt{\frac{a.r}{\mu(2a-r)}} \quad \ldots \quad (38\cdot4)$$

Substituting the value of r from $\frac{a(1-e^2)}{r} = 1 + e \cos\theta$,

$$\text{we get } v = \sqrt{\frac{2\mu(1+e\cos\theta)}{a(1-e^2)} - \frac{\mu}{a}} = \sqrt{\frac{\mu(1+e^2+2e\cos\theta)}{a(1-e^2)}}$$

$$\text{Hence } \frac{da}{dt} = \frac{2.a^2\sqrt{\mu}.\ \sqrt{1+e^2+2\ \cos\theta}}{\mu\ \sqrt{a(1-e^2)}} \cdot \text{R}$$

$$= \frac{2\text{R}}{n\sqrt{1-e^2}} \cdot \sqrt{1+e^2+2e\cos\theta}. \quad \ldots \quad (38\cdot5)$$

$$\frac{de}{dt} = 2\text{R}.\ (\cos\theta + e)\sqrt{\frac{a.\ (1-e^2)}{\mu(1+e^2)+2e\cos\theta)}}$$

$$= \frac{2\text{R}\sqrt{1-e^2}.\ (\cos\theta+e)}{n.\ a.\sqrt{1+e^2+2e\cos\theta}} \quad \ldots \quad (38\cdot6)$$

$$e\frac{dw}{dt} = \frac{2\text{R}.\ \sin\theta.\ \sqrt{a(1-e^2)}}{\sqrt{\mu\ (1+e^2+2e\cos\theta)}}$$

$$= \frac{2\text{R}\sqrt{1-e^2}}{n.\ a} \cdot \frac{\sin\theta}{\sqrt{1+e^2+2e\cos\theta}} \quad \ldots \quad (38\cdot7)$$

For a resisting force, we have to put $-\text{R}$ for R in the above equations. These formulæ were given by Tisserand.

3. It follows that for a resisting medium, $\frac{da}{dt}$ is always negative and varies with the anomaly θ. And so a diminishes incessantly after each revolution; n increases proportionately to the number of the revolutions. There is a secular diminution with parameter $a(1-e^2)$. But the eccentricity depends on the factor $\cos\theta+e$ and so $\frac{de}{dt}$ is sometimes positive and sometimes negative.

4. Each term of the product of the summations in §1 is of the form

$$-K\frac{v^p}{r^q} \quad \text{(See Routh's Dynamics, Art. 384, p. 247.)}$$

For this we get

$$\frac{1}{a}\frac{da}{dt}=\frac{-2K}{1-e^2}(1+e^2+2e\cos\theta).\frac{v^{p-1}}{r^q} \quad . \quad . \quad . \quad . \quad (38\cdot8)$$

$$\frac{de}{dt}=-2K.\ (\cos\theta+e)\frac{v^{p-1}}{r^q} \quad . \quad . \quad . \quad . \quad . \quad . \quad (38\cdot9)$$

$$e\frac{d\omega}{dt}=-2K.\ \sin\theta.\frac{v^{p-1}}{r^q}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (38\cdot10)$$

If we substitute $dt=\frac{r^2d\theta}{\sqrt{\mu a(1-e^2)}}$, we have

$$\frac{1}{a}\frac{da}{d\theta}=\frac{-2K'}{1-e^2}(1+e^2+2e\cos\theta)^{\frac{p+1}{2}}.\ (1+e\cos\theta)^{q-2} \quad . \quad (38\cdot11)$$

$$\frac{de}{d\theta}=-2K'(\cos\theta+e)\ (1+e^2+2e\cos\theta)^{\frac{p-1}{2}}.\ (1+e\cos\theta)^{q-2} \quad . \quad (38\cdot12)$$

$$e\frac{d\omega}{d\theta}=-2K'\sin\theta\,(1+e^2+2e\cos\theta)^{\frac{p-1}{2}}(1+e\cos\theta)^{q-2} \quad . \quad (38\cdot13)$$

$$K'=K\frac{\mu^{\frac{p-2}{2}}}{\{a(1-e^2)\}^{\frac{p}{2}+q-2}}=K\,n^{p-2}a^{p-1}(1-e^2)^{2-\frac{p}{2}-q}$$

where $\mu=n^3a^2$ . . . . (38·14)

SECTION II

A PARTICULAR CASE

1. For a particular planet K can be treated as a constant.

The density ρ may be regarded as a constant B_0 due to the inter-stellar matter + a function of r, the distance from the sun.

Now the resisting medium due to emanations from the sun as well as matter attracted by the sun would naturally have $\rho = \frac{B_2}{r^2}$, which may be assumed as approximately true.

$$\text{Hence} \qquad f(a, e, w) = K$$

$$\text{and} \qquad \psi(r) = B_0 + \frac{B_2}{r^2}$$

where obviously B_0 should be extremely small as compared to B_2 and may in the first instance be neglected.

As regards $F(v)$, it must naturally increase with v. For small velocities (up to sound) of material bodies passing through a dense medium like air, it was found by Bashforth[16] that if v be the velocity, measured in feet per second, d the diameter of the leadshot in inches, w the weight in pounds, then taking the resistance to be $\beta \frac{d^2}{w} \left(\frac{v}{1000}\right)^n$

$v < 850$	$n=2$	$\beta=61{\cdot}3$
$v > 850 < 1040$	$n=3$	$\beta=74{\cdot}4$
$v > 1040 < 1100$	$n=6$	$\beta=79{\cdot}2$
$v > 1100 < 1300$	$n=3$	$\beta=108{\cdot}8$
$v > 1300 < 2700$	$n=2$	$\beta=141{\cdot}5$

It may be a fair assumption to make that if the density of the medium decreases, and the velocity increases to several miles per second, $n = 1$ nearly.

Accordingly as a first approximation the law of resistance applicable to planets may be taken to be

$$R = -K.\frac{v}{r^2} \qquad \ldots \qquad (38{\cdot}15)$$

2. If $R = -K.\frac{v}{r^2}$, then $p=1$ and $q=2$.

Hence (1) $\frac{1}{a}\frac{da}{d\theta} = \frac{-2K^1}{1-e^2}(1+e^2+2e\cos\theta)$ where $K^1 = \frac{K}{\sqrt{\mu a(1-e^2)}}$.

$$\frac{\Delta a}{a} = -\frac{2K^1}{1-e^2}\Big[(1+e^2)\,\theta + 2e\sin\theta\Big]_0^{2\pi}$$

$$= \frac{-2K}{\sqrt{\mu a}(1-e^2)^{3/2}} 2\pi\,(1+e^2)$$

$$= \frac{2k\mu a\,.\,2\pi\,(1+e^2)}{h^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (38{\cdot}16)$$

(2) $$\frac{de}{d\theta} = -2K^1\,(\cos\theta + e) \qquad \text{where} \quad K^1 = \frac{K}{\sqrt{\mu a(1-e^2)}}$$

$$\therefore\ \Delta e = -2K^1 \Big[\sin\theta + e.\,\theta\Big]_0^{2\pi}$$

$$= -\frac{4\pi e.\,K}{\sqrt{\mu a(1-e^2)}} = -\frac{4\pi e}{h}.\,K \quad . \quad . \quad . \quad (38{\cdot}17)$$

(3) $$e\frac{d\omega}{d\theta} = -\,2K^1 \sin\theta$$

$$e\,\Delta\,\omega = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38{\cdot}18)$$

3. Generally, when the resistance is a function of v and r only it has no permanent effect on the longitude of the perihelion, but decreases both the semi-major axis and their eccentricity. The fact is that in such a case the tangential retardation causes the line of apsides to rotate backward during the one-half of the revolution and to rotate forward during the other half, the net result being nil.

The resisting medium has of course no component along the normal. But there is a normal component derived from the resultant force along the shifted direction. The normal component cannot affect the velocity, hence the semi-major axis is unchanged. A normal component rotates the line of apsides in one direction and then in the other direction of the two sections made by the latus rectum. Similarly, a normal force decreases the eccentricity during one-half of the revolution and increases it during the other half.

4. Now the tangential acceleration $-\,K.\frac{v}{r^2}$ can be resolved into two components one along the radius vector $= -K.\frac{v}{r^2}.\frac{\frac{dr}{dt}}{v} = -\frac{K}{r^2}\frac{dr}{dt}$. (38·19)

and the other along the transversal $= -K.\frac{v}{r^2}.\frac{\frac{rd\theta}{dt}}{v} = -\frac{K}{r}\frac{d\theta}{dt}$. (38·20)

Comparing these components with the additional terms in the equations of motion

$$\frac{d^2r}{dt^2} - r\left(\frac{d\theta}{dt}\right)^2 = -\frac{\mu}{r^2} - \frac{3\mu}{D^2}\frac{h^2}{r^4} + \frac{3\mu}{D}\frac{1}{r^2}\frac{dr}{dt}$$

and
$$\frac{1}{r}\frac{d}{dt}\left(r^2\frac{d\theta}{dt}\right) = \frac{\mu}{D}\cdot\frac{1}{r}\frac{d\theta}{dt}\left(1 - \frac{2}{D}\frac{dr}{d}\right)$$

it is apparent that the retardation caused by the resisting medium and the automatic acceleration can nearly balance each other if K is of the order $\frac{\mu}{D}$, which is natural as μ is the gravitational mass of the sun from which emanations proceed and D is the velocity at which emanations travel and maintain the density. The effect of the two additional terms on the eccentricity from Ch. 1. Sec. XII is

$$\triangle e = 6\pi e \frac{\mu}{Dh}$$

whereas the change in eccentricity due to the resisting medium as found in §2 (2) of this section is $\triangle e = -\frac{4\pi e}{h} K$ . . . . (38·21)

These will almost cancel each other if $\frac{3\mu}{2D} = K$ nearly.

The perturbations in the major axis will be similarly reduced. Thus the resistance can as a last resource fully counteract the automatic acceleration, reducing the observed changes in these elements if the radionic density be of the order 10^{-12}.

5. If the law of resistance involve a higher power of v, say v^2, then the density of the radionic medium near Mercury's orbit would be very considerably reduced, and be of the order 10^{-18}; and if it were of v^3, then the density would tally with the known density of the inter-stellar space 10^{-24}.

6. Now if the tangential resistance were not only a function of v and r but say $= -\frac{k}{r^2}(v+dv)^n$ where dv represents the increase in velocity along the tangent due to the shifted attractive force, then the transverse and radial components of the tangential resistance would be $-\frac{k}{r^2}(v^{n-1}+ndv)\,r\frac{d\theta}{dt}$ and $-\frac{k}{r^2}(v^{n-1}+ndv)\frac{dr}{dt}$ nearly. With appropriate values of k and n, the effect of the extra terms in the attractive forces which cause perturbations in the major axis, the eccentricity and even the longitude of the perihelion can be substantially reduced, and even made to vanish. This can certainly be the case if the law of resistance be a more complex function $f(v, dv)$, which will be considered later.

SECTION III

THE OBSERVED PERTURBATIONS

After taking immense pains for a long number of years, Newcomb (1895) calculated the values of the perturbations of the Four Minor Planets. He found out the observed values from calculation and also calculated the values theoretically according to Newton's law after taking into account the effect of the other planets also. The following table[17] gives his results so far as the changes in the eccentricity per century are concerned.

	Observation	Theory	Difference		
			Minimum	Maximum	Mean
Mercury	$+3''\cdot36$	$+4''\cdot24$	$-0''\cdot38$	$-1''\cdot38$	$-0''\cdot88$
Venus	$-9''\cdot46$	$-9''\cdot67$	$-0''\cdot10$	$+0''\cdot52$	$+0''\cdot21$
Earth	$-8''\cdot55$	$-8''\cdot57$	$-0''\cdot08$	$+0''\cdot12$	$+0''\cdot02$
Mars	$+19''\cdot00$	$+18''\cdot71$	$+0''\ 02$	$+0''\cdot56$	$+0''\cdot29$

Taking the mean values of the differences as the basis for consideration, it follows that in the case of Mars, Earth and Venus, the observed eccentricity is in excess of the theoretical one, while in the case of Mercury, it is deficient. The observations cannot be regarded as exact, but they can be accepted as tolerably accurate so far as the signs of the changes are concerned.

Now no existing theory, whether of Newton, Laplace or Einstein can explain an increase in eccentricity in a planetary orbit howsoever small Newcomb's observations of the orbits of Mars, Earth and Venus show that there are substantial increases. The known theories utterly fail to explain them. Newton's and Einstein's theories would give no increases, whereas Laplace's theory would give large decreases. These theories also fail to explain a change of sign for Mercury.

But the New Relativity Theory is the only theory which shows that there ought to be increases in the eccentricity. No doubt the increase predicted by it *prima facie* gives an increase of the order of $\frac{\mu}{h_0} = k = 10^{-4}$, which is rather large. The explanation of the resisting medium given

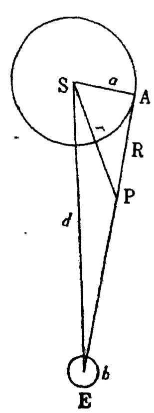
in Sec. II can meet this objection. For more distant planets, the resistance is small, and so the automatic acceleration still exceeds the retardation caused by the medium. But as Mercury is closer to the Sun, the resistance is greater, and the decrease in eccentricity due to the resistance is in excess of the increase due to the shifted direction, and the sign of the discrepancy in the case of Mercury is changed from positive to negative. This effect is observed still more markedly in the case of Enke's comet, which passes closer to the Sun, and its period is found to be appreciably reduced after each revolution.

Appendix to Chapter II, Section III

1. It will be shown in Chapter XI that there is a great uncertainty as to the extent of the spectral shift from the sun. The displacement is greater or less according as the level is higher or lower. The supposed agreement with the Relativity values for the centre and the edge is only for arbitrarily chosen levels, and these levels differ for the two. It seems that light loses in frequency as it is emitted from a higher level. Obviously light from the centre comes from a deeper level, the visible interior, than that from the edge, the visible exterior. The observed value for the centre is unreliable because of probable convection currents, and that from the edge because of its level. For the true values, the real test will be furnished by (1) light from the highest levels only, and (2) by taking the average of $M\,\Sigma\frac{a d\lambda}{\lambda}$ and not $Ma\,\frac{\Sigma d\lambda}{\Sigma\lambda}$.

2. If the path of light from an edge of the sun be considered to be straight, then following the method in Ch. II, Sec. III, pp. 27-28, the spectral shift can be calculated as follows:—

As the component of the velocity of gravitation along the path of light will be less than that of light, it will never overtake the light and the Doppler effect will be non-existent; only the intensity would diminish according to Newton's law.



Acceleration is $$f = -\frac{GM}{r^2}\cdot\frac{\sqrt{r^2-a^2}}{r} + \frac{Gm}{(\sqrt{d^2-a^2}-R)^2} \quad . \quad . \quad . \quad (39{\cdot}1)$$

Hence $$v^2 = v_0^2 + 2G.\int\left[\left\{-\frac{M}{r^2}\left(1-\frac{a^2}{2r^2}-\frac{1}{8}\frac{a^4}{r^4}\right)\right\} + \left\{\frac{m}{(\sqrt{d^2-a^2}-R)^2}\right\}\right]dR$$

$$=v^2_0+2G\left[\left\{\frac{M}{r}-\frac{Ma^2}{6r^3}-\frac{a^4}{40.r^5}\right\}+\frac{m}{\sqrt{d^2-a^2}-R}\right] \quad . \quad (39\cdot2)$$

At the Sun $v=v_s$, $r=a$ and $R=0$. Choose $r_0=c$ at ∞.

$$\therefore V^2_s = C^2+2\,G\left[\frac{M}{a}\left(1-\tfrac{1}{6}-\tfrac{1}{40}\right)+\frac{m}{d\left(1-\frac{a^2}{d^2}\right)^{\frac{1}{2}}}\right] \quad . \quad . \quad (39\cdot3)$$

At the Earth, $V=V_e$, $r=d-b$ and $R=\sqrt{d^2-a^2}-b$

$$\therefore V^2_e = C^2+2\,G\left[\frac{M}{d-b}(1-\tfrac{1}{6}-\tfrac{1}{40})+\frac{m}{b}\right] \quad . \quad . \quad (39\cdot4)$$

As $\lambda=v.T$, it follows that if T is nearly the same for similar atoms, then $\lambda\propto v$.

$$\text{Hence } \frac{\lambda_s}{\lambda_e}=\frac{V_s}{V_e}=\frac{1+\frac{G}{c^2}\left[\frac{97}{120}\cdot\frac{M}{a}+\frac{m}{d}\cdot\left(1+\frac{1}{2}\frac{a^2}{d^2}\right)\right]}{1+\frac{G}{c^2}\left[\frac{97}{120}\,\frac{M}{d-b}+\frac{m}{b}\right]} \quad . \quad . \quad . \quad (39\cdot5)$$

$$=\frac{97}{120}\times1\cdot00000211 \text{ nearly}$$

$$=1\cdot00677 \text{ for blue light} \quad . \quad . \quad . \quad . \quad . \quad . \quad (39\cdot6)$$

In such a case the displacement at the limb = ·00676

3. If the path is hyperbolic, then obviously $V^2=\frac{2\mu}{r}+\frac{\mu}{A}$. The spectral shift from the edge would then be nearly $\frac{\mu}{a}$, the same as that in the case of the light from the centre.

4. On Laplace's conception of the opposite velocity the spectral shift would be several times Enistein's value.

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A THEORY OF CONTINUOUS ABSORPTION SPECTRA OF DIATOMIC MOLECULES

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A large amount of experimental work has been done in this laboratory and elsewhere on the continuous absorption spectra of diatomic molecules[1] though a satisfactory theory is still lacking. As is well known there are two types of continuous absorption. In the first type we have generally a band absorption which gradually passes over into a continuous absorption on the violet side. Such absorption is shown by nonpolar diatomic molecules like the halogens,[2] nitrogen[3] and oxygen.[4] An explanation of this kind of absorption is afforded with the aid of Franck-Condon diagrams and is quite well known.[5]

The second type of continuous absorption is shown by most of the halides of the alkalis[6] and saturated oxides[7] and sulphides.[8] Here we do not get any band absorption but one or more regions of continuous absorption. These, too, are explained on the Franck-Condon diagram in which the upper U_r/r curve is assumed to be of repulsive type.[9]

A theory of the pure band absorption spectrum in the case of the molecules of the first type was given by Hutchisson[10] from the wave mechanical point of view and further extended by Langstroth[11] to the case of excitation of band spectra of diatomic molecules by electrons. In his paper Hutchisson calculated the transition probabilities between two representative points on the lower and upper curves of the U_r/r diagram representing the molecule in its normal and excited conditions. The molecules are regarded as purely harmonic oscillators. In another paper, Hutchisson[12] extended his calculations to non-harmonic oscillators as well, by applying the theory of perturbation.

Hutchisson further compared the calculated intensities with those observed experimentally. The cases taken were the absorption spectra of Na_2, K_2, I_2, H_2 and the emission spectrum of H_2. The agreement is not very good between the calculated and observed intensities in most of

these molecules in spite of the large number of adjustable constants. It is, however, better for those bands which are due to transitions between states possessing very low vibration quantum numbers. The extension of Langstroth[11] improves this agreement between the observed and calculated values of the intensities of the emission spectra of the N^2 molecule.

The case of continuous band absorption in the case of molecules of the first type was treated from the wave mechanical point of view by Gibson, Rice and Bayliss[13] in a supplement to the paper describing the experimental part of their work on the continuous absorption of chlorine. Their model of the molecule in the normal state was an anharmonic oscillator of the Kratzer type. For the upper state, the Schrödinger equation was taken to be

$$\frac{d^2\psi}{dr^2}+\frac{8\pi^2\mu_0}{h^2}\left(E-V-\frac{j(j+1)h^2}{8\pi^2\mu_0 r^2}\right)\psi=0$$

The essential point in this paper is the choice of the potential energy function $V(r)$. This was taken empirically as being given by the formula

$$V(r)=V_\infty+\left[h^2\left(\omega^2-\frac{1}{4}\right)\Big/8\pi^2\mu_0\rho^2\right]$$

where $\rho=r-r_0$; V_∞, ω and r_0 being constants. It is clear that such a function cannot represent the form of the potential function representing the upper state, but Gibson and others justify the choice by the remark that the expression for $V(r)$ represents the upper part of the curve to the left of the minimum of the curve for the lower state, which alone is of consequence in such calculations. A slightly different method was given by Stueckelberg[14] for calculating the continuous absorption of O_2.

No attempt has yet been made for calculating the continuous absorption of the molecules of the second type. In another paper the present author will report the results of his experimental work on a quantitative determination of the absorption spectra of the HCl and HBr molecules. The object of the present paper is to report a calculation of the intensity of continuous absorption by this type of molecules from wave mechanics. The lower curve is represented by an anharmonic oscillator, but for the upper curve, the potential energy U_r is represented by $U_r = A + De^{-ar}$. In a previous paper[15] it has been shown that the vibration eigen-values for such a state are continuous and the values of the vibration eigen-functions are different from zero for those points which lie above the horizontal asymptote of the Franck-Condon curve for that state. This is in

agreement with the usual finding by workers of this laboratory that in the case of molecules of polar type the continuous absorption starts rather sharply at a point which corresponds to the dissociation of the molecule into two normal atoms. The upper curve may, therefore, be taken to correspond to the potential energy of a normal H and a normal Cl as they approach each other from infinity

There is some difference of opinion whether the hydrogen halides can be regarded as ionic or atomic;[16] but the present investigation is not affected by such considerations.

1. Fundamental considerations regarding absorption coefficients.

We shall begin with the investigation of the optical absorption of a diatomic molecule on the lines of wave mechanics. Since in all such experiments where the continuous absorption spectrum of substances is observed the quantity to be measured is the absorption coefficient, the fundamental expression for this quantity will first be given. The absorption coefficient is defined as

$$k_\nu = \frac{{}^\nu\varepsilon \ln 10}{6{\cdot}06 \times 10^{20}} = -\frac{1}{N} \cdot \frac{d \ln I}{dl} \quad . \quad . \quad . \quad . \quad (1)$$

where I is the intensity of the incident light of a particular frequency ν, N the number of molecules per c.c., l the distance traversed by the light in cms., ${}^\nu\varepsilon$ the total absorption coefficient of light of frequency ν given by the formula

$$I = I_0 \times 10^{{}^\nu\varepsilon cd}.$$

Here I_0 is the intensity of the incident light, I the intensity of the transmitted light, d the length of the absorption column in cms. and c the concentration of the gas in moles per litre.

The molecules of the gas are usually distributed initially among the vibrational and rotational states of the normal electronic state. Therefore

$$\varepsilon = N_0\varepsilon_0 + N_1\varepsilon_1 + N_2\varepsilon_2 + \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $N_0 + N_1 + N_2 + \ldots . = 1$, and N_v is the fraction of the total number of molecules which exist in the state with vibration quantum number v at a temperature T; $\varepsilon_0, \varepsilon_1, \ldots .$ are the partial absorption coefficients appropriate to the various vibrational levels. If E_v represents the energy difference between the state v and the lowest state $v=0$, equation (2) becomes[17]

$$\varepsilon = \left[\varepsilon_0 + \varepsilon_1 e^{-E_1/\kappa \times T} + \varepsilon_2 e^{-E_2/\kappa \times T} + \ldots\right] \Big/ \sum_v e^{-E_v/\kappa \times T} \quad . \quad . \quad (3)$$

where $\kappa = 1 \cdot 372 \times 10^{-16}$.

Now ${}^{\nu}k$ is given by the relation

$${}^{\nu}k \; N = \sum_{\alpha''} \sum_{\alpha'} P_{\alpha''\alpha'} \quad N_{00} e^{-E_{\alpha''}/1 \cdot 372 \times 10^{-16} \times T} \quad . \quad . \quad . \quad (4)$$

where α'' and α' are abbreviations for the various quantum numbers of the lower and upper electronic states of the molecule, N_{00} is the number of molecules per c.c. in the state of lowest energy, $E_{\alpha''}$ is the energy in ergs of the state α'' measured from the state with the lowest energy, T is the absolute temperature, and the constant $1 \cdot 372 \times 10^{-16}$ ergs per degree absolute temperature used in (3) and (4) is the Boltzmann's constant. $P_{\alpha''\alpha'}$ is defined as the absorption coefficient per molecule referring to an incident beam of one photon crossing unit area per second per unit frequency range. It is given by the formula[18]

$$P_{\alpha''\alpha'} = \frac{8\pi^3 \nu}{3hc} \left| D_{\alpha''\alpha'} \right|^2 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where the matrix component $D_{\alpha''\alpha'}$ is given by

$$D_{\alpha''\alpha'} = \int \psi''_{\alpha''} \cdot D \cdot \psi'_{\alpha'} \, d\tau \quad . \quad . \quad . \quad . \quad (6)$$

$\psi''_{\alpha''}$ and $\psi'_{\alpha'}$ being the eigen-functions of the lower and upper electronic states of the molecule respectively and D being the electric moment.

The wave-function of the normal state of the molecule will, according to Born and Oppenheimer,[19] be approximately of the form

$$\theta_j\,(\theta) \cdot \; R_v\,(r) \cdot \; \chi\,(x)$$

where $R_v\,(r)$ represents the vibrational eigen-function, $\theta_j\,(\theta)$ the rotational eigen-function and $\chi\,(x)$ the electronic eigen-function. We get a similar product for the upper state. The equation (6) is, thus, composed of a product of three matrix components; rotational, vibrational and electronic. The electric moment will be a linear function of x and r, the electronic and nuclear coordinates. Since we are treating the band arising from

same electronic transition the integration over the electronic coordinates may be supposed to be carried out giving

$$D_{a''a'} = L_{j''}^{j'} \int D_\chi \cdot R''(r) \cdot R'(r)\, d\tau \quad . \quad . \quad . \quad . \quad (7)$$

where D_χ is the result of integrating D with the two electronic factors of the wavefunction over the electron coordinates, $L_{j''}^{j'}$ is the result of integrating the two rotational functions. D_χ is, thus, an effective electric moment of the molecule for the electron jump in question. Without great error,[20] it can be regarded as essentially constant for the range of r in which the radial functions $R(r)$ are appreciably different from zero.

The rotational matrix components $\left| L_{j''}^{j'} \right|^2$ have been calculated by London and Hönl.[21] The value thus obtained is $(2j''+1)$, all possible transitions from the rotational state with quantum number j'' being considered.

For the calculation of the vibrational matrix component we have to evaluate both the upper and lower vibration wave-functions of the molecule.

2. Evaluation of the eigenfunction of the lower state.

To evaluate the vibrational wavefunction $R''(r)$ for the lower state, we write the Schrödinger equation as

$$\frac{d^2R}{dr^2} + \frac{8\pi^2\mu}{h^2}\left[E - V - \frac{j(j+1)\,h^2}{8\pi^2 r^2 \mu} \right] R = 0 \quad . \quad . \quad . \quad (8)$$

μ being the reduced mass.

We shall omit all dashes in this section for the sake of convenience.

For $j=0$, we take the potential energy V to be given, after Gibson and others,[13] by the formula $-\frac{\gamma}{\rho} + \frac{\beta}{\rho^2}$ where $\rho = r - r_0$. The molecule is, thus, an anharmonic oscillator of the Kratzer's type. The constants r_0, γ and β can be so chosen as to give the best agreement with the Morse curve in the region near the minimum of potential energy curve. Putting $\frac{8\pi^2\mu}{h^2} E = -b_v^2$ and $\frac{8\pi^2\mu}{h^2}\beta = m\,(m-1)$, the quantum condition becomes

$$\frac{8\pi^2\mu\gamma}{h^2 \cdot 2b_v} - m = v$$

where $v = 0, 1, 2, \ldots$

Putting $\xi = 2b_v\rho$, $2m-1=\alpha$ and $r \cdot R_v(r) = F_v(r)$, the normalised eigenfunctions $F_v(r)$ are given by

$$F_v(r) = \left[\frac{v\,!}{2m+2v}\right]^{\frac{1}{2}} \left[\Gamma(2m+v)\right]^{-\frac{3}{2}} e^{-\xi/2}\,\xi^m \cdot L^{\alpha}_{v+\alpha}(\xi) \quad . \quad . \quad (9)$$

where $L^{\alpha}_{v+\alpha}(\xi)$ is the Laguerre polynomial given by the expression

$$e^{i\pi(\alpha+v)} \cdot \frac{\Gamma(1+\alpha+v)}{v\,!}\left[\xi^v - \frac{(\alpha+v)v}{1\,!}\xi^{v-1} + \frac{(\alpha+v)\,(\alpha+v-1)\,v\,(v-1)}{2\,!}\xi^{v-2} + \;.\;.\;.\right].$$

If the normalisation is made with respect to variable ξ instead of r, the above expression has to be multiplied by $(2b_v)^{\frac{1}{2}}$.

3. Evaluation and normalisation of the eigenfunctions for the upper state.

Let us now find out $R'_{v'j'}(r)$. For the sake of convenience we may omit the dash in this section and write the Schrödinger equation as

$$\frac{d^2F}{dr^2} + \frac{8\pi^2\mu}{h^2}(W - D\,e^{-2ar})\,F = 0$$

where $F = r \cdot R(r)$

Its solution has already been given as[15]

$$F = J_n(z)$$

where $z = \lambda e^{-ar}$; $\dfrac{8\pi^2\mu D}{a^2} = -\lambda^2 = C^2$ and $\dfrac{8\pi^2\mu W}{a^2} = -n^2 = B^2$; $J_n(z)$ being a Bessel function of order n and argument z.

First of all we have to normalise this function. As the corresponding eigenvalues are continuous the usual formula for normalisation obtained by Schrödinger, *viz.*,

$$N^2\int RR^*\,r^2 dr = 1$$

does not hold good. For the continuous case the normalising condition was worked out by Hellinger,[22] Weyl[23] and Sommerfeld.[24] In the general form defining normalisation and expressing the orthogonal property at the same time

$$\mathop{\mathcal{L}}_{\Delta W \to 0} \int \varphi(B)\,F(B, r) \int_{\Delta W} \varphi(B')\,F^*(B', r)\,dW'\,dr = {}^{0}_{1} \quad . \quad . \quad (10)$$

since we have $F = r \cdot R(r)$ and the interval $\triangle W$ encloses the point W. Since the only significant contribution to the value of the integral comes from those values of B′ which lie in the infinitesimal spread corresponding to $\triangle W$, it is evident that we can replace the region of integration $\triangle W$ by the interval $0 \to \infty$. Assuming the legitimacy of the inversion of the order of integration we can write the same integral as

$$\int_0^\infty \varphi(B)\, \varphi'(B) \cdot \left[\int F(B, r)\, F^*(B', r)\, dr \right] dW' \quad . \quad . \quad (10a)$$

To find out this condition we shall first consider the integral

$$\int F(B, r) \cdot F^*(B', r)\, dr$$

we have $F(B, r) = J_{iB}(iCy)$ and $F^*(B', r) = J_{-iB'}(-iCy)$, where $y = e^{-ar}$.

Therefore $dy = -ay\, dr$ and $dr = -\dfrac{dy}{ay}$

$$\int_{-\infty}^{+\infty} F \cdot F^*\, dr = -\frac{1}{a} \int_0^\infty \frac{J_{iB}(iCy) . J_{-iB}(-iCy)}{y} dy$$

Since $$J_n\left(xe^{\frac{\pi i}{2}}\right) = e^{\frac{n\pi i}{2}} J_n(x)$$

(see *Theory of Bessel Function*, by G. N. Watson, p. 175)

we have $$\int_{-\infty}^{+\infty} F \cdot F^*\, dr = -\frac{1}{a} \int_0^\infty \frac{J_{iB}\left(Cye^{\frac{i\pi}{2}}\right) . J_{(-iB')}\left(Cye^{\frac{-i\pi}{2}}\right)}{y} dy$$

which after some work reduces to the expression

$$-\frac{e^{-\frac{\pi}{2}(B+B')}}{a} \cdot \frac{\Gamma(1)\Gamma\left(\frac{i}{2}\overline{B-B'}\right)}{2\Gamma\left(1-\frac{iB'}{2}-\frac{iB}{2}\right)\Gamma\left(1+\frac{iB}{2}-\frac{iB'}{2}\right)\Gamma\left(1+\frac{iB}{2}-\frac{iB'}{2}\right)}$$

(see Watson's *Theory of Bessel Function*, p. 403).

Since $\Gamma(1+z) = z\,\Gamma(z)$; $\Gamma(z)\,\Gamma(1-z) = \dfrac{\pi}{\sin \pi z}$ and $\Gamma(1) = 1$

(see Whittaker and Watson: *Modern Analysis*, pp. 237, 239)

we get the above expression reduced to the form

$$-\frac{e^{-\frac{\pi}{2}(B+B')}}{\pi a} \cdot \frac{2 \sin i \frac{\pi}{2} (B+B')}{(B+B')(B'-B)} \cdot$$

Now $\quad B^2 = -\nu^2 = \frac{8\pi^2\mu}{a^2h^2} W$ and $B'^2 = -\nu'^2 = \frac{8\pi^2\mu}{a^2h^2} W'$

therefore $\qquad dW' = \frac{a^2h^2}{4\pi^2\mu} B'dB'.$

Putting $i\nu$ for B, and $i\nu'$ for B', and substituting the value of dW', expression (10 *a*) is obtained in the following form, with the difference that the integration is carried over the region $\triangle W$.

$$\mathcal{L}_{-\frac{a^2h^2}{4\pi^2\mu}d\nu \to 0} \frac{2N}{\pi a} \cdot \frac{2a^2h^2}{8\pi^2\mu} \int_{-\frac{a^2h^2}{4\pi^2\mu}d\nu} N' \frac{\nu' e^{-\frac{\pi}{2} i(\nu+\nu')} \cdot \sin \frac{\pi}{2}(\nu+\nu')}{\nu'^2 - \nu^2} d\nu'. \quad . \quad (11)$$

Since $\qquad \sin \frac{\pi}{2}(\nu+\nu') = \frac{e^{i\frac{\pi}{2}(\nu+\nu')} - e^{-i\frac{\pi}{2}(\nu+\nu')}}{2i}$

the expression under the integral becomes

$$\frac{1}{4i\nu} \int_{-\frac{a^2h^2}{4\pi^2\mu}d\nu} N' \frac{1-e^{-i\pi(\nu+\nu')}}{(\nu'-\nu)} d\nu'$$

where $N' = \varphi(B')$, and $\nu+\nu'$ = its approximate value 2ν. If now, in this expression, the region of integration is extended so as to become infinite we get the above expression as

$$\frac{1}{4i\nu} \int_{0}^{-\infty} \varphi(i\nu') \frac{1-e^{-i\pi(\nu+\nu')}}{\nu'-\nu} d\nu' \quad . \quad . \quad , \quad (11a)$$

This is an improper integral if $\varphi(i\nu')$ is taken to be a constant and our first object is to choose $\varphi(i\nu')$ in such a manner that the integral

coming in (11*a*) remains convergent. It can be seen that a suitable form of $\varphi\,(i\nu')$ is

$$\left(\frac{\nu'}{\nu}\right)^{-\frac{1}{2}}\frac{\delta}{e^{-i\pi(\nu+\nu')}-1},$$ where δ is a constant. The expression

(11*a*) then becomes $$\frac{\delta}{4i\nu}\int\limits_{-\infty}^{0}\frac{\left(\frac{\nu'}{\nu}\right)^{-\frac{1}{2}}d\nu'}{\nu\left(1-\frac{\nu'}{\nu}\right)}$$

Putting $-\dfrac{B'}{B}=x$, we have the above expression as

$$-\frac{\delta}{4i\nu}\int\limits_{0}^{\infty}\frac{x^{-\frac{1}{2}}\,dx}{(1+x)}$$

which on integration amounts to

$$-\frac{\delta}{4i\nu}\;\frac{\Gamma\left(\frac{1}{2}\right)\Gamma\left(\frac{1}{2}\right)}{\Gamma\,(1)}$$

(see Peirce: *A Short Table of Integrals*, Ginn and Co., p. 62, No. 482).

which is equal to $-\dfrac{\delta\pi}{4B}$.

The expression (11) becomes

$$-\frac{ah^2\,\delta}{8\pi^2\mu B}\,\varphi\,(B)=-\frac{ah^2\delta^2}{8\pi^2\mu B}\cdot\frac{1}{e^{-2\pi B}-1}$$

which is equal to unity according to the condition for normalisation.

or $$\delta=\left(e^{-2\pi B}-1\right)^{\frac{1}{2}}\sqrt{\frac{8\pi^2\mu B}{ah^2}}$$

or $$\varphi\,(B)=\left(e^{-2\pi B}-1\right)^{-\frac{1}{2}}\sqrt{\frac{8\pi^2\mu B}{ah^2}}$$

This expression gives the normalising factor. Having thus normalised the wave function, the ψ-function behaves as if it were of a discreet state and its weight factor would be unity.[25]

Therefore, in order that it becomes normalised, each eigenfunction F (B, r) will have to be multiplied by this function φ (B), which, in what follows, we shall denote by N.

4. Calculation of the transition probability.

Having normalised the wavefunction for the unstable state we have now to determine the vibrational matrix component

$$M^{v'j'}_{v''j''} = \int_{-\infty}^{+\infty} F''_{v''j''} \cdot F'_{v'j'}\, dr \quad . \quad . \quad . \quad . \quad , \tag{12}$$

We have seen above that the various eigenfunctions represented by $F''_{v''j''}$ are a sum of several factors of the type $\rho^{\mu}\, e^{-b\rho}$, each multiplied by a constant. The wavefunction of the unstable state is

$$N\ J_{iB}\left(i\, C\, e^{-ar_0} e^{-a\rho}\right).$$

To calculate the vibrational matrix component, we have to evaluate integrals of the type

$$\int_{-\infty}^{+\infty} N\, \rho^{\mu} e^{-b\rho} J_{iB}\,(iC\, e^{-ar_0} e^{-a\rho})\, d\rho \quad . \quad . \quad . \quad . \tag{13}$$

where $\rho = r - r_0$ as already assumed above.

$$\text{Since } y = e^{-ar},\ e^{ar_0}y = e^{-a\rho},\ e^{ar_0}dy = -a e^{ar_0} y\, d\rho$$

$$\therefore\ d\rho = -\frac{dy}{ay}$$

$$\text{Further } \log\,(e^{ar_0}\, y) = -a\rho$$

$$\text{or} \qquad \rho = -\frac{1}{a} \log y\, e^{ar_0}$$

$$\text{also} \qquad e^{-b\rho} = e^{-a\rho \frac{b}{a}} = y^{\frac{b}{a}}\, e^{br_0}$$

The integral (13), therefore, becomes

$$\frac{1}{a^2}\, e^{br_0} \cdot N \int_{0}^{\infty} (\log y e^{ar_0})^{\mu}\, y^{\frac{b-a}{a}}\, J_{iB}\,(iGy)\, dy. \quad . \quad . \tag{13a}$$

where $G = C\, e^{2ar_0}$.

Since both y and e^{ar_0} are very slightly smaller than unity, we have ye^{ar_0} very slightly differing from unity. Putting $ye^{ar_0} = 1 - x$, where x is a very small quantity, we have,

$$\left[\log ye^{ar_0}\right]^{\mu}=(-1)^{\mu}\left(x+\frac{x^2}{2}\right)^{\mu}$$

$$=\left(-\frac{3}{2}\right)^{\mu}\left(1+y^2e^{2ar_0}\right)^{\mu}$$

$$=\left(-\frac{3}{2}\right)^{\mu}\left[1+\frac{\mu y^2e^{2ar_0}}{3}+\frac{\mu(\mu-1)}{2!}\cdot\frac{y^4e^{4ar_0}}{3^2}+\frac{\mu(\mu-1)(\mu-2)}{3!}\cdot\frac{y^6e^{6ar_0}}{3^3}\right]$$

Since $\int_0^{\infty} J_n(lt)\cdot t^{\theta-1}dt$

$$=\frac{\left(\frac{1}{2}l\right)^n\Gamma(\theta+n).}{l^{\theta+n}\Gamma(1+n)}\,{}_2F_1\left(\frac{n+\theta}{2},\ \frac{1-\theta+n}{2};\ 1+n;\ 1\right),$$

(see G.N. Watson's *The Theory of Bessel Function*, p. 385)*
the integral (13a) becomes

$$\left(-\frac{3}{2}\right)^{\mu}\cdot\frac{Ne^{br_0}}{a^2}\left[\frac{\left(\frac{1}{2}\right)^{iB}\Gamma\left(iB+\frac{b}{a}\right)}{(iG)^{b/a}\,\Gamma(1+iB)}\cdot\right.$$

$$_2F_1\left(\frac{iB+\frac{b}{a}}{2},\ \frac{1+iB-\frac{b}{a}}{2};\ 1+iB;\ 1\right)$$

$$+\frac{\mu e^{2ar_0}}{3}\cdot\frac{\left(\frac{1}{2}\right)^{iB}\Gamma\left(iB+\frac{b}{a}+2\right)}{(iG)^{b/a+2}\,\Gamma(1+iB)}\cdot$$

$$_2F_1\left(\frac{iB+\frac{b}{a}+2}{2},\ \frac{iB-\frac{b}{a}-1}{2};\ 1+iB;\ 1\right)$$

* The symbol F which is used henceforth for hypergeometric functions must not be confused with the earlier use of F in §§ 3 and 4, where F denoted $r\times$radial part of the ψ-function.

$$+\frac{\mu(\mu-1)}{2!}\cdot\frac{e^{4ar_0}}{3^2}\cdot\frac{\left(\frac{1}{2}\right)^{iB}\Gamma\left(iB+\frac{b}{a}+4\right)}{(iG)^{b/a+4}\,\Gamma(1+iB)}\cdot$$

$$ {}_2F_1\left(\frac{iB+\frac{b}{a}+4}{2},\ \frac{iB-\frac{b}{a}-3}{2};\ 1+iB;\ 1\right)$$

$$+\frac{\mu(\mu-1)(\mu-2)}{3!}\cdot\frac{e^{6ar_0}}{3^3}\cdot\frac{\left(\frac{1}{2}\right)^{iB}\Gamma\left(iB+\frac{b}{a}+6\right)}{(iG)^{b/a+6}\,\Gamma(1+iB)}\cdot$$

$$ {}_2F_1\left(\frac{iB+\frac{b}{a}+6}{2},\ \frac{iB-\frac{b}{a}-5}{2};\ 1+iB;\ 1\right)\Bigg]$$

${}_2F_1(\alpha, \beta; \gamma; 1)$ is a hypergeometric function and is given as

$$\sum_{s=0}^{\infty}\frac{\alpha_s\cdot\beta_s}{s!\cdot\gamma_s}$$

where $\alpha_s=\alpha(\alpha+1)\ \ldots\ (\alpha+s-1)$, $\alpha_0=1$.

As has been shown by Gibson and others that although the vibrational matrix depends to some extent on the rotational quantum number of the stable state, we shall make a negligible error if we take it independent of j.

We have, therefore, with the aid of (4), (5) and (6)

$$^{v}k\mathrm{N}=\sum\frac{8\pi^3\nu}{3hc}\,\mathrm{D}^2{}_{n''n'}\cdot(2j+1)\cdot\mathrm{N}_{00}\left|\mathrm{M}_{v''j''}^{v'j'}\right|^2\cdot e^{-\mathrm{E}_{v''j''}/\kappa\mathrm{T}}$$

The values of $\left|\mathrm{M}_{v''j''}^{v'j'}\right|^2$ are given below for (*a*) transitions from $v''=0$ vibrational level to the upper continuous state, and (*b*) transitions from $v''=1$ vibrational level to the upper continuous state.

$$(a)\quad\left|\mathrm{M}_0^{v'}\right|^2=\left|\left(-\frac{3}{2}\right)^m\cdot\mathrm{N}\frac{e^{b_0r_0}}{a^2}\cdot\frac{(2b_0)^{m+\frac{1}{2}}}{\{\Gamma(2m+1)\}^{\frac{1}{2}}}\left[\frac{\left(\frac{1}{2}\right)^{iB}\Gamma\left(iB+\frac{b_0}{a}\right)}{(iG)^{b_0/a}\,\Gamma(iB+1)}\cdot\right.\right.$$

$$ {}_2F_1\left(\frac{iB+\frac{b_0}{a}}{2},\ \frac{1-\frac{b_0}{a}+iB}{2};\ 1+iB;\ 1\right)$$

$$+\frac{me^{2ar_0}}{3}\cdot\frac{\left(\frac{1}{2}\right)^{iB}\Gamma\left(iB+\frac{b_0}{a}+2\right)}{(iG)^{b_0/a+2}\,\Gamma(1+iB)}\cdot$$

$$_2F_1\left(\frac{iB+\frac{b_0}{a}+2}{2},\ \frac{iB-\frac{b_0}{a}-1}{2};\ 1+iB;\ 1\right)$$

$$+\frac{m\,(m-1)e^{4ar_0}}{18}\cdot\frac{\left(\frac{1}{2}\right)^{iB}\Gamma\left(iB+\frac{b_0}{a}+4\right)}{(iG)^{b_0/a+4}\,\Gamma(1+iB)}\cdot$$

$$_2F_1\left(\frac{iB+\frac{b_0}{a}+4}{2},\ \frac{iB-\frac{b_0}{a}-3}{2};\ 1+iB;\ 1\right)$$

$$+\frac{m(m-1)\,(m-2)e^{6ar_0}}{162}\cdot\frac{\left(\frac{1}{2}\right)^{iB}\Gamma\left(iB+\frac{b_0}{a}+6\right)}{(iG)^{b_0/a+6}\,\Gamma(1+iB)}\cdot$$

$$_2F_1\left(\frac{iB+\frac{b_0}{a}+6}{2},\ \frac{iB-\frac{b_0}{a}-5}{2};\ 1+iB;\ 1\right)\Bigg]\Bigg|^2$$

$$(b)\qquad \left|M_1^{v'}\right|^2=\left|\left(\frac{3}{2}\right)^m\cdot N\,\frac{e^{b_1r_0}}{a^2}\cdot\frac{(2b_1)^{m+\frac{1}{2}}\cdot 2m}{\{[\Gamma(2m+1)].\ (2m+2)\}^{\frac{1}{2}}}\left[\frac{\left(\frac{1}{2}\right)^{iB}\Gamma\left(iB+\frac{b_1}{a}\right)}{(iG)^{b_1/a}\,\Gamma(iB+1)}\cdot\right.\right.$$

$$_2F_1\left(\frac{iB+\frac{b_1}{a}}{2},\ \frac{1-\frac{b_1}{a}+iB}{2};\ 1+iB;\ 1\right)$$

$$+\frac{me^{2ar_0}}{3}\cdot\frac{\left(\frac{1}{2}\right)^{iB}\Gamma\left(iB+\frac{b_1}{a}+2\right)}{(iG)^{b_1/a+2}\,\Gamma(1+iB)}\cdot$$

$$_2F_1\left(\frac{iB+\frac{b_1}{a}+2}{2},\ \frac{iB-\frac{b_1}{a}-1}{2};\ 1+iB;\ 1\right)$$

$$+\frac{m(m-1)}{18}\, e^{4ar_0} \cdot \frac{\left(\frac{1}{2}\right)^{iB} \Gamma\left(iB+\frac{b_1}{a}+4\right)}{(iG)^{b_1/a+4}\ \Gamma(1+iB)} \cdot$$

$$ {}_2F_1\left(\frac{iB+\frac{b_1}{a}+4}{2},\ \frac{iB-\frac{b_1}{a}-3}{2};\ 1+iB;\ 1\right)$$

$$+\frac{m(m-1)(m-2)}{162}\, e^{6ar_0} \cdot \frac{\left(\frac{1}{2}\right)^{iB} \Gamma\left(iB+\frac{b_1}{a}+6\right)}{(iG)^{b_1/a+6}\ \Gamma(1+iB)} \cdot$$

$$ {}_2F_1\left(\frac{iB+\frac{b_1}{a}+6}{2},\ \frac{iB-\frac{b_1}{a}-5}{2};\ 1+iB;\ 1\right)\Bigg]$$

$$-\frac{(2b_1)^{m+\frac{1}{2}} \cdot 2b_1}{\{(2m+2)\,\Gamma(2m+1)\}^{\frac{1}{2}}} \cdot \left(-\frac{3}{2}\right)^{m+1} \cdot N \cdot \frac{e^{b_1 r_0}}{a^2} \left[\frac{\left(\frac{1}{2}\right)^{iB} \Gamma\left(iB+\frac{b_1}{a}\right)}{(iG)^{b_1/a}\ \Gamma(1+iB)} \cdot\right.$$

$$ {}_2F_1\left(\frac{iB+\frac{b_1}{a}}{2},\ \frac{1-\frac{b_1}{a}+iB}{2};\ 1+iB;\ 1\right)$$

$$+\frac{(m+1)}{3}\, e^{2ar_0} \cdot \frac{\left(\frac{1}{2}\right)^{iB} \Gamma\left(iB+\frac{b_1}{a}+2\right)}{(iG)^{b_1/a+2}\ \Gamma(1+iB)} \cdot$$

$$ {}_2F_1\left(\frac{iB+\frac{b_1}{a}+2}{2},\ \frac{iB-\frac{b_1}{a}-1}{2};\ 1+iB;\ 1\right)$$

$$+\frac{m(m+1)}{18}\, e^{4ar_0} \cdot \frac{\left(\frac{1}{2}\right)^{iB} \cdot \Gamma\left(iB+\frac{b_1}{a}+4\right)}{(iG)^{b_1/a+4}\ \Gamma(1+iB)} \cdot$$

$$ {}_2F_1\left(\frac{iB+\frac{b_1}{a}+4}{2},\ \frac{iB-\frac{b_1}{a}-3}{2};\ 1+iB;\ 1\right)$$

$$+\frac{(m+1)\,(m)(m-1)e^{6ar_0}}{162}\cdot\frac{\left(\frac{1}{2}\right)^{iB}\Gamma\left(iB+\frac{b_1}{a}+6\right)}{(iG)^{b_1/a+6}\,\Gamma(1+iB)}.$$

$$_2F_1\left(\frac{iB+\frac{b_1}{a}+6}{2},\ \frac{iB-\frac{b_1}{a}-5}{2};\ 1+iB;\ 1\right)\Bigg].$$

By measuring the actual absorption coefficient of the sample of gas, and having determined the various constants involved in the potential energy of the molecule in its normal electronic state from the data of its absorption in the infra-red, we are able to calculate the various constants involved in the potential energy of the molecule in its upper unstable state.

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THE NITROGEN ATOM AND THE MOLECULE

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SUMMARY

This paper contains a detailed report of the Spectrum of Atomic and Molecular Nitrogen, and reviews all the recent work on the various systems of bands. An account is given of the recent work of Herzberg who obtains the value 7·34 ± ·02 volts for the heat of dissociation of N_2 into two normal $N(^4S_{\frac{3}{2}})$-atoms, from discussion of predissociation data. Discussion is given also of Mulliken's work who obtains the value 7·28 volts from Lozier's electron-bombardment results. It is shown that the identification of the origin of some bands is doubtful. Plans for further work, particularly in the Schumann region are discussed. This paper is preliminary to a paper on the Active Modification of Nitrogen.

1. Introduction

Nitrogen is one of the most interesting elements in the periodic table. As is well known, it does not usually react with other elements, but this inertness is only apparent, as it forms a large number of compounds: witness for example the fact that it forms with oxygen no less than five different oxides all of which are fairly stable. The apparent inertness of the nitrogen gas is rather deceptive. It was long believed by chemists that the nitrogen atom is very active. In fact the very inertness of the N_2 molecule was ascribed to the fact that the two atoms of nitrogen grip each other so strongly that the N_2 molecule receives an inert gas-like electronic structure and becomes chemically inactive.

It was found by E. P. Lewis[1] at the beginning of the present century that nitrogen gas through which a disruptive discharge is passed becomes active, that is to say, the luminescence persists for considerable time even when the discharge is stopped; and the luminous nitrogen gas produces a number of chemical reactions of which the ordinary gas is incapable. So a discussion of the properties of atomic and molecular nitrogen cannot but be of interest to the Physicists and Chemists alike.

At the present time, there is a tendency to interpret all physical and chemical properties in terms of the electronic structure of the atom. In this article we shall summarise the properties of the nitrogen atom and N_2 molecule from this point of view and try to show how this enables us to throw light on the properties of the gas.

2. Atomic Nitrogen

The constitution of the N atom is given by $1s^2 2s^2 2p^3$. From this we can easily construct the various spectroscopic levels. These are shown in Table 1. The value obtained spectroscopically[2,3] are also shown in the same table.

Table 1.—Term values of the arc spectrum of nitrogen.

Configuration	Terms	Term values
$2s^2.2p^3$	$^4S_{\frac{3}{2}}$	117345
	$^2D_{\frac{5}{2}}$	
	$^2D_{\frac{3}{2}}$	98143
	$^2P_{\frac{1}{2}}$	
	$^2P_{\frac{3}{2}}$	88537
$2p^2.3s$	$^4P_{\frac{1}{2}}$	34059·5
	$^4P_{\frac{3}{2}}$	34025·7
	$^4P_{\frac{5}{2}}$	33979·0
	$^2P_{\frac{1}{2}}$	31213·6
	$^2P_{\frac{3}{2}}$	31121·8
	$^2D_{\frac{3}{2}}$	
	$^2D_{\frac{5}{2}}$	17681·0
$2s.2p^4$	$^4P_{\frac{5}{2}}$	29235·5
	$^4P_{\frac{3}{2}}$	29191·6
	$^4P_{\frac{1}{2}}$	29172·0
$2p^2.3p$	$^2S_{\frac{1}{2}}$	23762·7
	$^4D_{\frac{1}{2}}$	22572·8
	$^4D_{\frac{3}{2}}$	22550·2
	$^4D_{\frac{5}{2}}$	22512·9
	$^4D_{\frac{7}{2}}$	22461·9
	$^4P_{\frac{1}{2}}$	21868·5
	$^4P_{\frac{3}{2}}$	21850·1
	$^4P_{\frac{5}{2}}$	21811·8
	$^4S_{\frac{3}{2}}$	20593·3
	$^2D_{\frac{3}{2}}$	20556·8
	$^2D_{\frac{5}{2}}$	20480·8
	$^2P_{\frac{1}{2}}$	19574·9
	$^2P_{\frac{3}{2}}$	19539·2
	$^2D_{\frac{3}{2}}$	6823·1
	$^2D_{\frac{5}{2}}$	6799·2
	$^2P_{\frac{1}{2}}$	5050·2
	$^2P_{\frac{3}{2}}$	5024·2
$2p^2.4s$	$^4P_{\frac{1}{2}}$	13726·9
	$^2P_{\frac{3}{2}}$	13676·9
	$^4P_{\frac{5}{2}}$	13608·2
	$^2P_{\frac{3}{2}}$	13117·6
	$^2P_{\frac{1}{2}}$	13202·8
$2p^2.3d$	$^2P_{\frac{3}{2}}$	12729·6
	$^2P_{\frac{1}{2}}$	12690·1
	$^4F_{\frac{3}{2}}$	12688
	$^4F_{\frac{5}{2}}$	12660·8
	$^4F_{\frac{7}{2}}$	12626·5
	$^4F_{\frac{9}{2}}$	12577
	$^2F_{\frac{5}{2}}$	12534·1
	$^2F_{\frac{7}{2}}$	12462·3
	$^4P_{\frac{1}{2}}$	12481
	$^4P_{\frac{3}{2}}$	12455
	$^4P_{\frac{5}{2}}$	12388
	$^4D_{\frac{5}{2}}$	12334·3
	$^4D_{\frac{7}{2}}$	12325·5
	$^2D_{\frac{3}{2}}$	12224·2
	$^2D_{\frac{5}{2}}$	12200·7
$2p^2.4p.$	$^2S_{\frac{1}{2}}$	10866·4
	$^4D_{\frac{1}{2}}$	10584·5
	$^4D_{\frac{3}{2}}$	10564·9
	$^4D_{\frac{5}{2}}$	10528·9
	$^4D_{\frac{7}{2}}$	10474·3
	$^4P_{\frac{1}{2}}$	10362·3
	$^4P_{\frac{3}{2}}$	10346·7
	$^4P_{\frac{5}{2}}$	10306·0
	$^4S_{\frac{3}{2}}$	9897·8

The table shows that the normal term of nitrogen is a quartet S-term $^4S_{\frac{3}{2}}$ which has rather very high value. In fact, the ionisation potential of N is equal to 14·5 volts and is actually greater than that of oxygen which normally ought to have a higher ionisation potential. This is due to the higher multiplicity of the term. The principal lines of nitrogen due to the transitions $(2p^3-2p^23s)$, $(2p^3-2p^23d)$ are mostly in the ultra-violet. The lines arising from the next transition $(2p^23s-2p^23p)$ $(2p^23p-2p^23d)$ are in the infra-red. Hence nitrogen makes a very poor show in the visible spectrum.

The fundamental electronic structure of N $1s^22s^22p^3$ gives rise to five terms $^4S_{\frac{3}{2}}$, $^2D_{\frac{3}{2},\frac{5}{2}}$, $^2P_{\frac{1}{2},\frac{3}{2}}$. The values of all terms are known with precision According to the Selection Principles, we do not usually expect any line due to intertransition between these levels, but it is well-known that the rule is broken under certain unusual circumstances, *i.e.*, when the gas is subjected to electric discharge in a highly attenuated state, *e.g.*, in the upper atmosphere or in nebula. Such lines are known for O, for the green auroral line $\lambda5577$ is due to $2p^4(^1D_2-{}^1S_0)$ and the red lines $\lambda6300, \lambda6364$ are due to $2p^4(^3P_{1,2}-{}^1D_2)$. The wavelengths of the corresponding forbidden lines of N are shown in the table below, but the lines have not yet been obtained either in the auroral or the night sky spectrum. (There is a doubtful identification of $^4S-{}^2D$, $\lambda5202$ by Slipher and Sommer in the auroral spectrum, see *Naturwissenschaft*, 1929, p. 802)

Table 2.—Forbidden lines of nitrogen.

S. No.	Transition	Frequency cm⁻¹	Wavelength A°.U.	Energy in Volts
1	$2p^3\ ^4S_{\frac{3}{2}}-2p^3\ ^2P_{\frac{3}{2},\frac{1}{2}}$	28840	3467·4	3·56
2	$2p^3\ ^4S_{\frac{3}{2}}-2p^3\ ^2D_{\frac{5}{2}}$	19223	5202·1	2·37
3	$2p^3\ ^4S_{\frac{3}{2}}-2p^3\ ^2D_{\frac{3}{2}}$	19231	5199·9	
4	$2p^3\ ^2D_{\frac{5}{2}}-2p^3\ ^2P_{\frac{3}{2},\frac{1}{2}}$	9617	10398·3	1·19
5	$2p^3\ ^2D_{\frac{3}{2}}-2p^3\ ^2P_{\frac{3}{2},\frac{1}{2}}$	9606	10410·2	

The lines $^2D-{}^2P$ which correspond to the green line are in the long infra-red, and as observations extend to this region, we shall probably obtain this line some day in the spectrum of the aurora and the night sky. The lines $^4S-{}^2P$ also are in convenient regions, but they are expected to be weak. No reliable identifications of these lines are known in the aurora.

3. Molecular Spectrum of Nitrogen

Though a large amount of work has been done on the molecular spectrum of nitrogen, yet much remains to be done to clear up the observed data while there is still more to be discovered and our knowledge is far from being complete. The present knowledge regarding the

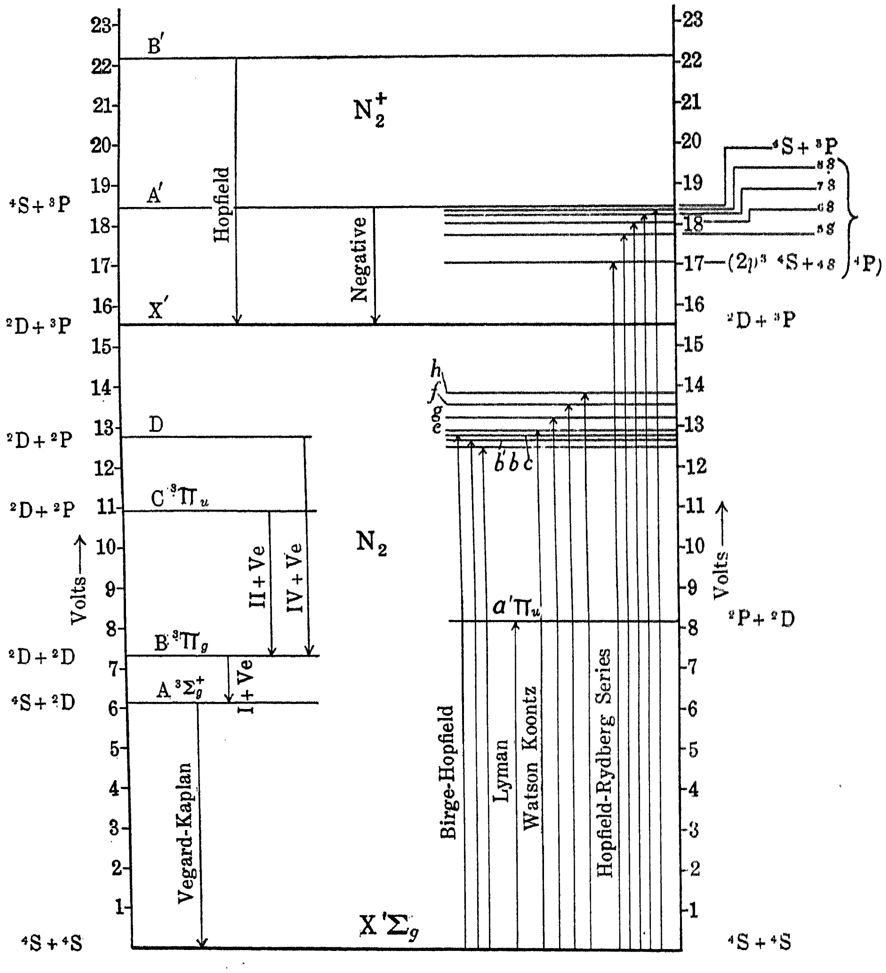

Fig. 1.—(By the kind courtesy of 'The National Institute of Sciences of India').

molecular spectrum of this gas can be summarised in the form of Table 3 which together with Figs. 1 & 2 gives a fairly complete representation of its spectrum, as far as it is known.

The normal nitrogen atom having the electron configuration $1s^2\ 2s^2\ 2p^3$ possesses ^4S, ^2D and ^2P levels. The molecule of nitrogen

can be built with two atoms in any of these three spectroscopic states A large number of molecular levels result from the different combinations and are given in the Table 4.

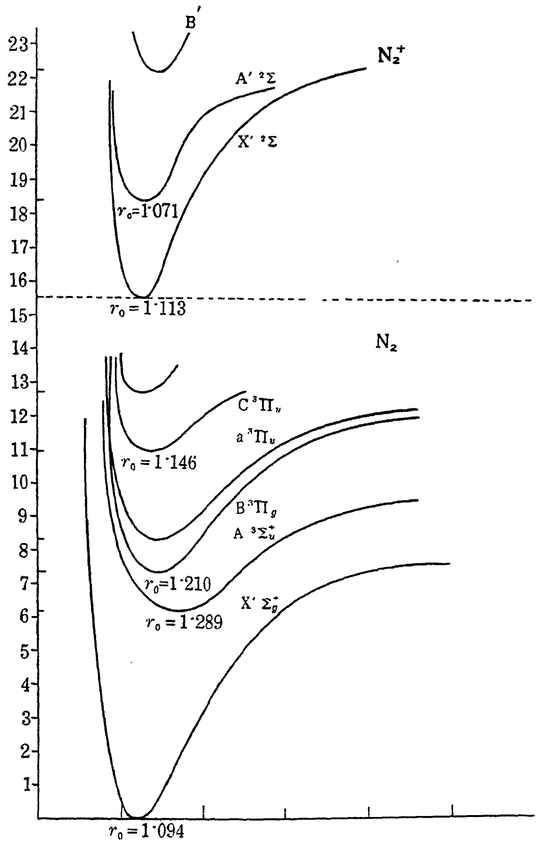

Fig. 2

Table 4.—Predicted levels of N_2

S. No.	Combination	Terms Calculated	Terms Observed
1	$^4S+{}^4S$	$^1\Sigma$, $^3\Sigma$, $^5\Sigma$, $^7\Sigma$.	$^1\Sigma$
2	$^2D+{}^2D$	$^1\Sigma$,$^1\Pi$,$^1\Delta$,$^1\Phi$,$^1\Gamma$,$^3\Sigma$,$^3\Pi$,$^3\Delta$,$^3\Phi$,$^3\Gamma$	$^3\Pi$
3	$^2P+{}^2P$	$^1\Pi$, $^1\Delta$, $^1\Phi$, $^3\Pi$, $^3\Delta$, $^3\Phi$	
4	$^4S+{}^2D$	$^3\Sigma$, $^3\Pi$, $^3\Delta$, $^5\Sigma$, $^5\Pi$, $^5\Delta$	$^3\Sigma$
5	$^4S+{}^2P$	$^3\Pi$, $^5\Pi$	
6	$^2D+{}^2P$	$^1\Sigma$, $^1\Pi$, $^1\Delta$, $^1\Phi$, $^3\Sigma$, $^3\Pi$, $^3\Delta$, $^3\Phi$	$^1\Pi$,$^3\Sigma$ or $^3\Delta$,$^3\Pi$

Table 3.—Spectroscopic constants of

Molecule	Molecular constants of N_2 and N_2^+								
	State	E_e + cm^{-1}	$E_{(0,0)}$ volts	ω_e cm^{-1}	$x_e \omega_e$ cm^{-1}	D volts	B_0 cm^{-1}	α cm^{-1}	r_e A.U.
N_2^+	$B'\ {}^2\Sigma_u^+$	54024	6·64	2173·2	10·43	...	...	...	...
	$A'\ {}^2\Sigma_u^+$	25566·0	3·15	2396·22	24·070	3·7 (Birge)	2·073	0·025	1·071
	${}^2\Pi_u$	...	·65	...	...	...	...	...	1·02
	$X'\ {}^2\Sigma_g^+$	0	0	2191·02	16·196	6·31 (Mulliken)	1·920	0·02	1·113
N_2	$D\ {}^3\Sigma$?	103511·0	12·77	...	...	...	...	...	...
	$C\ {}^3\Pi_u$	88946·1	10·98	2044·70	26·047	1·10	1·8202	0·0200	1·1468
	h	...	...	...	...	...	...	...	...
	f	...	...	...	...	...	...	...	...
	g	...	...	...	...	...	...	...	...
	e	...	...	...	...	...	...	...	...
	c	104394·6 104318·7	12·87	...	...	...	...	...	...
	$b'\ {}^1\Pi_u$	103677·7	12·79	...	...	...	1·147	...	...
	b	101469·2	12·52	...	...	...	...	...	...
	$a\ {}^1\Pi_u$	68962·7	8·51	1692·28	13·318	5·7	1·632	0·021	
	$B\ {}^3\Pi_g$	59293·0	7·32	1732·84	14·437	4·76	1·66 (I+*ve*) 1·6342 (II+*ve*)	0·023 (I+*ve*) 0·0177 (II+*ve*)	1·20 (I+*ve*) 1·2107 (II+*ve*)
	$A\ {}^3\Sigma_g^+$	49774·4	6·14	1446·46	13·93	3·56	1·440	0·013	1·289
	$X\ {}^1\Sigma_g^+$	0	0	2359·60	14·445	7·34	1·998 (Lyman) 1·992 (Raman)	0·018	1·094

different levels of N_2 and N_2^+

Brief description of band systems	Transition	$\nu_{0,0}$
Hopfield-Watson-Koontz bands λ1721—λ2051 $\nu=54024+2173{\cdot}2\,(v'+\tfrac{1}{2})-10{\cdot}43\,(v'+\tfrac{1}{2})^2-0{\cdot}017\,(v'+\tfrac{1}{2})^3$ $-2207{\cdot}16\,(v''+\tfrac{1}{2})-16{\cdot}136\,(v''+\tfrac{1}{2})^2-0{\cdot}040\,(v''+\tfrac{1}{2})^3$.	$B'\,^2\Sigma_u^+ \rightarrow X'\,^2\Sigma_g^+$	54024
Negative bands λ2900 —λ5900 $\nu=25566{\cdot}0+2396{\cdot}22v'-24{\cdot}070v'^2-0{\cdot}6365v'^2$ $-0{\cdot}04949v'^4-(2191{\cdot}02v''-16{\cdot}196v''^2-0{\cdot}0400v''^3)$	$A'\,^2\Sigma_u^+ \rightarrow X'\,^2\Sigma_g^+$	25566·0
No band system is so far observed. Only knowledge gained is from perturbations.		
Fourth positive bands λ 2904—λ2256 $\nu=44218{\cdot}0-(1718{\cdot}40v''-14{\cdot}437v''^2)$	$D\ ^3\Sigma \rightarrow B\ ^3\Pi$	44218·0
Second positive bands λ5438—λ2692 $\nu=29670{\cdot}6+(2020{\cdot}00v'-26{\cdot}40v'^2-1{\cdot}158v'^3-0{\cdot}5542v'^4)$ $-(1719{\cdot}64\,v''-14{\cdot}47\,v''^2)$	$C^3\Pi \rightarrow B\ ^3\Pi$	29670·6
Watson-Koontz	$h \leftarrow X\ ^1\Sigma_g^+$	
Watson-Koontz	$f \leftarrow X\ ^1\Sigma_g^+$	
Watson-Koontz	$g \leftarrow X\ ^1\Sigma_g^+$	
Watson-Koontz	$e \leftarrow X\ ^1\Sigma_g^+$	
Birge-Hopfield λ 1075·1—λ 1310·3 $\nu=\left.\begin{matrix}104394{\cdot}6\\104318{\cdot}7\end{matrix}\right\}-(2345{\cdot}16\,v''-14{\cdot}445\,v''^2)$	$c \leftarrow X\ ^1\Sigma_g^+$	104394·6 104318·7
Birge-Hopfield bands λ 1057·7—λ 1644·1 $\nu=103677{\cdot}7-(2345{\cdot}16\,v''-14{\cdot}445\,v''^2)$	$b' \leftarrow X\ ^1\Sigma_g^+$	103677·7
Birge-Hopfield bands λ1008·6—λ 1438·0 $\nu=101469{\cdot}2-(2345{\cdot}16\,v''-14{\cdot}445\,v''^2$	$b \leftarrow X\ ^1\Sigma_g^+$	101469·2
Lyman bands λ 1205·3—λ 1804 $\nu=68962{\cdot}7+(1678{\cdot}96\,v'-13{\cdot}318\,v'^2-0{\cdot}0354\,v'^3)$ $-(2345{\cdot}16\,v''-14{\cdot}445\,v''^2)$	$a'\Pi_u \leftarrow X'\ ^1\Sigma_g^+$	68962·7
First positive bands λ 5029—λ 14700 $\nu=9518{\cdot}59+(1718.40v'-14{\cdot}437v'^2)-(1446\ 44v''-13{\cdot}929v''^2)$	$B^3\Pi_g \rightarrow A\ ^3\Sigma_g^+$	9518·59
Vegard—Kaplan bands $\nu=49774{\cdot}4+(1446{\cdot}46v'-13{\cdot}93v'^2)-(2345{\cdot}16v''-14{\cdot}45v''^2)$	$A^3\Sigma_g^+ \rightarrow X\ ^1\Sigma_g^+$	49774·4
Raman Bands.		

Out of such a large number of molecular levels only a few levels can be identified with the known levels of N_2 and even in such cases great uncertainty prevails because the products of dissociation cannot be determined with certainty.

However, from Fig. 1 it will be clear that nitrogen bands arise out of two systems of levels which are respectively denoted as A, B, C, D and X, a, b, b', c, etc. The levels denoted by X and the small letters form singlet system and those represented by capital letters (except X) are triplets. For a long time no intercombination between these two systems was known, just as in the case of ortho and para levels of helium. But recently Vegard obtained an intercombination $A^3\Sigma - X^1\Sigma$ in the luminescence of solid nitrogen. Kaplan[4] obtained some of these bands in a discharge through gaseous nitrogen showing that triplet levels combine with singlet levels under certain special conditions.

4. Lyman Bands of Nitrogen

(*i*) Lyman Bands lying in the ultra-violet in the region λ 1206 – λ 2090 are degraded towards the red. They result from the transition $a - X$ where the level a lies 68962·7 cm^{-1} above the ground state X. This band system appeared in the earlier observations of Schumann,[5] Lyman,[6] Birge and Hopfield.[7,8] For a time, it was suspected as being due to NO because Sponer[9] found that the upper levels of the γ-bands of NO had apparently the same vibrational constants as the lower level of this system. Great interest was aroused in the analysis of these bands when Sponer[10] observed them in absorption in cold nitrogen gas. On an extensive band analysis Birge and Hopfield[11] gave the following formula for the band heads:—

$$\nu_{head} = 68962{\cdot}7 + (1678{\cdot}96\, v' - 13{\cdot}318\, v'^2 - {\cdot}0354\, v'^3) - (2345{\cdot}16\, v'' - 14{\cdot}445\, v''^2) \quad \ldots \quad (1)$$

Appleyard[12] employed a 21 ft. grating for studying the rotational analysis of some of these bands. He found that the bands (5 – 13) and (5 – 14) were the only ones developed sufficiently for a rotational analysis. The values of the rotational constants obtained by him are given below:—

$$B'_5 = 1{\cdot}5207 \pm 0{\cdot}001\ cm^{-1}$$
$$B''_{13} = 1{\cdot}7625 \pm 0{\cdot}001\ cm^{-1}$$
$$B''_{14} = 1{\cdot}7424 \pm 0{\cdot}001\ cm^{-1}$$

Appleyard denotes the upper levels as $^1\Pi_u$.

Watson and Koontz[13] by passing a condensed discharge in tank Helium made an extensive study of the molecular spectrum of nitrogen and employed a 10 ft. normal incidence vacuum grating spectrograph which gave a dispersion of 5·5 A° per mm. in the first order. They made the rotational analysis of (0, 1) (0, 4) (1, 5), (1, 6) (1, 7) and (2, 8) bands and gave the following values for the rotational constants:—

$$B'_0 = 1{\cdot}632 \pm 0{\cdot}002 \text{ cm}^{-1} \quad \alpha' = 0{\cdot}021$$
$$B''_0 = 1{\cdot}998 \pm 0{\cdot}002 \text{ cm}^{-1} \quad \alpha'' = 0{\cdot}018$$

The B''_0 values for the normal $^1\Sigma_g^+$ state of this band is in confirmity with Rasetti's[14] value of $1{\cdot}992 \pm 0{\cdot}005$ cm^{-1} which was obtained from the rotational Raman spectrum of nitrogen gas. The rotational lines of each of the P and Q branches exhibit alternation of intensity. The ratio of the intensities is 2 : 1 which shows that the nuclear magnetic moment = 1.

Recently Kaplan[15] reported many new members of the Lyman-Birge-Hopfield system. With the small dispersion of E31 spectrograph he identified the bands (5, 15) (6, 16) (7, 17) (8, 18) (9, 19) (10, 20) (11, 21); (8, 17) (9, 18) (10, 19) (11, 20); (9, 20) (10, 21) (11, 22). The band (11, 22) is located at λ 2425 A°. Kaplan observed that for bands whose v'-value exceeds 9, $\Delta v' \gtreqless 9$ sequence there is a sudden drop in the intensity and the bands become diffuse. This suggests that predissociation starts at this stage, and since the energy of $v'=8$ is 10·06 volts it corresponds to a dissociation of the N_2-molecule into ^4S and ^2D (*vide* infra).

Many attempts have been made to find out the nature of the levels of the atoms into which a particular molecular level will dissociate if it is allowed to vibrate to an infinite distance. These attempts can only be made by the interpolation formula as was first attempted by Birge and Sponer[16] but these interpolation results are never trustworthy, *e.g.*, Birge and Sponer[16] found that D for the state X=11·6 volts.

We have

$$D = \int_0^{v_{max}} \omega(v)\, dv \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and for $\omega(v)$ we use the formula

$$\omega(v) = \omega_0 - 2\,\omega_0\, v + \ldots = \frac{1}{h}\,\frac{\partial E}{\partial v} \quad . \quad . \quad . \quad (3)$$

The heat of dissociation of the normal N_2-molecule has been obtained on other grounds (*vide* infra) and found to be 7·34 volts. If the level X is one of the levels arising from the combination ($^4S_{\frac{3}{2}}$, $^4S_{\frac{3}{2}}$) this value is too large. There are strong reasons to believe that the electrons of the component atoms are in these states for the normal N_2-molecule is almost inert like Neon $^1S_0$. This is very easily explained by saying that the spins of the three electrons in one atom are all in the same direction and spins of other three electrons in the second atom are in the opposite direction so that each component atom is in $^4S_{\frac{3}{2}}$ state The extrapolation formula therefore gives values very wide off the mark

The heat of dissociation of the upper state *a* is found to be 5·7 volts. If according to Kaplan the upper state dissociates into ^4S and ^2D nitrogen atoms the difference AB of Fig. 3 is equal to $^4S-^2D$ of nitrogen atom, which from Table 1 is 19202 cm^{-1} or 2·3 volts. From the excitation potential and heat of dissociation of the upper state AB$=$8·51$+$5·7$-$7·34$=$ 6·87 volts. Hence Kaplan's scheme of dissociation of the upper state does not appear to be in harmony with the observed data. Now if the upper state is regarded as dissociating into ^2D and ^2P nitrogen atoms then the difference AB$=$($^4S-^2D$)$+$ ($^4S-^2P$) of nitrogen which is about 6 volts. This scheme of dissociation is also supported from the absorption experiments in cold N_2-gas. The absorption of the Lyman-Birge-Hopfield bands leading to the transition ($X\longrightarrow a$) is found to be very weak. In fact, Lyman states that an absorption vessel 9·14 mm. in length filled with N_2 at atmospheric pressure produces a very slight absorption, extending continuously from λ 1800 to λ 1250. Leifson[91, 92] states that a layer 5 mm. thick at one-fifth of the atmospheric pressure (equivalent to a light path of 1 mm.) produces no noticeable absorption. If the absorption corresponded to the dissociation from X ($^4S+^4S$) to a($^4S+^2D$) the absorption would be much stronger. This may be contrasted with the absorption of

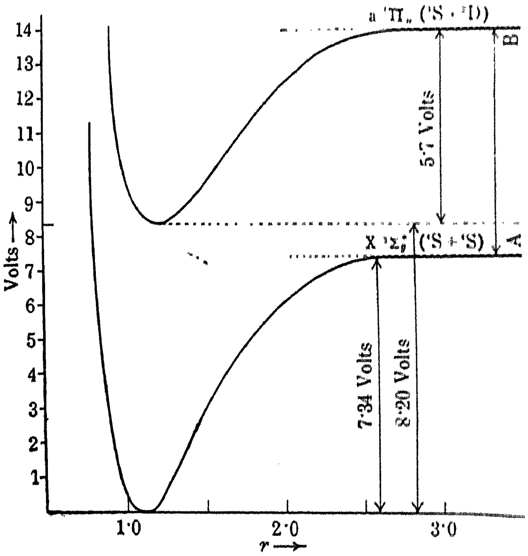

Fig. 3

Runge-Schumann bands which are obtained with a cell 25 mm. in length and with pressures varying between 18 mm. and 240 mm. The Runge-Schumann bands correspond to the transition ($^3P+^3P$) $X^3\Sigma_g^-$ to ($^3P+^1D_2$) $B^3\Sigma_u^-$, *i.e.*, the electron transits from ^3P to $^1D_2$. If the *a*-state of N_2 corresponded to $^4S+^2D$ the transition would be similar, *i.e.*, the electron passing from ^4S to ^2D, and the absorption would have been quite heavy as in O_2. The small absorption of oxygen can be explained by saying that the *a*-state is made up of $^2D+^2P$, *i.e.*, it involves two electron forbidden transitions and is therefore very slight. The argument is not quite conclusive for the $^4S+^2D$ combination of N_2 which gives $A(^3\Sigma)$ should also give a singlet $^1\Sigma$-term, and the transition from ($^4S+^4S$) X to ($^4S+^2D$) $^1\Sigma$ would be attended with heavy absorption in the same region as the Lyman bands. If the Lyman bands do not correspond to these transitions what are we to think of their correct origin?

5. Birge-Hopfield and Watson-Koontz, ground state Progressions and Hopfield Rydberg series

In the region λ1008–λ1644 Birge and Hopfield[8,11] obtained a number of bands in emission which on analysis were found to arise from combination of the normal level X with three other upper levels called *b*, *b′*, *c*. For these bands the v''-values varied from 0 to a large number but v' had only a single value which is still undetermined. Thus on analysis only the ground state vibrational progressions were apparent as shown below:—

$$b\text{-series } \nu_{head}=101469{\cdot}2-(2345{\cdot}16\, v''-14{\cdot}445\, v''^2) \quad \quad (4)$$

$$b'\text{-series } \nu_{head}=103677{\cdot}7-(2345{\cdot}16\, v''-14{\cdot}445\, v''^2) \quad \quad (5)$$

$$c\text{-series } \nu_{head}=\left.\begin{matrix}104394{\cdot}6\\104318{\cdot}6\end{matrix}\right\}-(2345{\cdot}16\, v''-14{\cdot}445\, v''^2) \quad \quad (6)$$

Inspite of the fact that the three progressions lie in a short span of 650A, their lack of similarity in appearance and visible change in intensity distribution for the members of one progression with those of the other helped considerably in assigning their individual progressions.

It was observed by Birge and Hopfield that *b′*-series failed to appear in certain plates probably due to a change in conditions of the excitation of the discharge tube. They were inclined to ascribe it to NO rather than to N_2 but Watson and Koontz[13] found an alternation in intensity of the branches, while making a rotational analysis. This

speaks in favour of N_2 as the emitter of bands. These bands should be obtained in absorption, but the experiments have not yet been tried. From the formulæ (4), (5) and (6) it is clear that the v'-values for the three progressions are not yet known so that the vibrational ground frequency ν_e is undetermined and therefore the electronic levels cannot be fixed correctly. Assuming the upper level to be in the hypothetical state of zero vibration the values for the levels b, b' and c have been fixed up. It is easy to see that this is far from satisfactory. Watson and Koontz computed the value of the rotational constant B for the b' level for $v'=14, 15$ and 16 and took $B'_0=1{\cdot}147$ as the average of B values for the above levels. This is nearly half the rotational constant for the ground state, so that the minimum of the potential energy curve for b' level is shifted towards the right. The vibrational number of the upper level has therefore some high value and bands with different v'-values should be obtained. V. Culanovsky[102] has done the rotational analysis of some of the bands of b'-series.

Let v' be the vibration quantum number of the level actually obtained. Then we have

$$\left.\begin{array}{lll} \text{for } b & \nu=\nu_{eb} & +[\omega'_e\,(v'+\tfrac{1}{2})-x'_e\,\omega'_e\,(v'+\tfrac{1}{2})^2+\cdots\cdots]-\cdots \\ b' & \nu=\nu_{eb}' & +[\omega'_e\,(v'+\tfrac{1}{2})-x'_e\,\omega'_e\,(v'+\tfrac{1}{2})^2+\cdots\cdots]-\cdots \\ c & \nu=\nu_{ec} & +[\omega'_e\,(v'+\tfrac{1}{2})-x'_e\,\omega'_e\,(v'+\tfrac{1}{2})^2+\cdots\cdots]-\cdots \end{array}\right\} \quad . \quad . \quad (7)$$

so that unless ω' and v' are known the value of the electronic levels cannot be found out.

It is quite possible that one of these levels is a higher Rydberg sequence of the level a, so that

$$a \qquad \mathrm{N}\ 2p^3\ {}^4\mathrm{S}_{\frac{3}{2}},\ \mathrm{N}\ 2p^3 3s\cdots$$

$$b \text{ or } b' \text{ or } c \text{ is } \mathrm{N}\ 2p^3\ {}^4\mathrm{S}_{\frac{3}{2}},\ \mathrm{N}\ 2p^3 4s\cdots$$

but the B′-value for a and b' do not tally as we should expect But Watson and Koontz conclude that b is a ${}^1\Pi_u$-term. This is in favour of the view that b' arises as sketched above. But more work is necessary before any conclusion can be reached.

Recently in a systematic search for new nitrogen bands in the vacuum-ultra-violet region, arising from higher to the ground-level transition such that the electronic level of the upper state is a Rydberg sequence to that of the level a. Watson and Koontz[18] found several other ground state progressions which they named as d, e, f, g and h. These bands have not yet been obtained in absorption. They have reported that

experiments with the object of obtaining these bands in absorption are in progress and suggest that low gas pressure will favour the appearance of these bands in the high frequency region of investigation. For the sake of completeness and the interesting nature of these progressions we give below a table of the frequencies of the band heads of the *d*, *e*, *f*, *g* and *h*-series together with v''-values as given in Watson's original paper.[13]

Table 5.—Watson and Koontz Progressions

v''	*d*	v''	*e*	v''	*f*	v''	*g*	v''	*h*
3	98237·0	10	83874·5	1	107860·6	1	106606·5	5	101414·0
4	95999·3	11	81831·5	2	105548·8	2	104306·3	6	99226·0
5	93781·7	12	79814·4	3	103270·0	3	102018·4	7	97071·1
6	91597·7	13	77836·0	4	101044·9	4	99801·4	8	94953·5
7	89449·2			5	98829·8	5	97591·1	9	92836·2
8	87322·0			6	96641·8	6	95398·4	11	88713·6
9	85218·9			7	94489·4	7	93247·0	12	86721·8
10	83150·7			8	92355·2	8	91136·3	13	84710·4
11	81115·6			9	90265·3	9	89027·6	14	82769·9
				11	86176·0	11	84942·4		
				12	84151·4	12	82899·7		
						13	80919·9		

No definite conclusion regarding the origin of these bands can be reliably given because proper data are at present not available.

Some time back Hopfield[17] reported the presence of a Rydberg sequence of bands in the region below λ750. With helium as the source of light he obtained five bands λ723·2, 694·2, 681·7, 675·2 and 671·2 in absorption and another set of four bands λ715·2, 690·9, 680·1 and 674·3A° in emission only. Hopfield's data closely fit in the following Rydberg's formula:—

$$\nu = 151240 - \frac{R}{(m - 0{\cdot}092)^2} \quad \ldots \quad (8)$$

where $m=3, 4, 5, 6, 7, \ldots\ldots$ The point worthy of note is that the emission Rydberg series converges to the same limit as the absorption Rydberg series. The limit=151240 cm^{-1}=18·67 Volts. This limit is identified with the ionisation of N_2 molecule to form an excited state of N_2^+. R. S. Mulliken[18] has discussed in detail the theoretical reasons which lend support to the view that the excited state into which N_2-molecule finds itself at the limit of the Rydberg series found by Hopfield is the excited level A′ of the ionised molecule. We can suppose that the bands originate from the transitions between upper levels which are formed of two nitrogen atoms, one in $2p^3$ ^4S-state and the other in $2p^2ns$, ^4P state ($n=1, 2, 3, \ldots$) and the ground level $X^1\ \Sigma_g^+$ of nitrogen composed of two $2p^3$ ^4S atoms. This supposition seems to be justifiable for we find that $\Delta\nu$ for the upper band heads correspond to the $\Delta\nu$ of the successive $2p^2ns$ ^4P-terms of the neutral atom of nitrogen as shown in Table 6 and Fig. 1. In

Table 6.—Hopfield Absorption Rydberg Series.

Absorption Rydberg Series.					Terms in the Arc Spectrum of Nitrogen		
S. No.	λ A°.U	V volts.	ν cm^{-1}	Δ ν cm^{-1}	Designation	Term cm^{-1}	Δ ν cm^{-1}
1.	723	17·05	138274·5		$2p^2\ 4s\ ^4P$	13608	
				5778			6191
2.	694	17·78	144052·5		$2p^2\ 5s\ ^4P$	7417	
				2750			2755
3.	681	18·11	146802·4		$2p^2\ 6s\ ^4P$	4662	
				1305			1,460
4.	675	18·28	148107·3		$2p^2\ 7s\ ^4P$	3198	
				883			
5.	671	18·39	148990·2				

the above table band λ723 is identified with the transition ($2p^3\,^4S+2p^2\,4s\,^4P$)←($2p^3\,^4S+2p^3\,^4S$). From this we conclude that the fundamental band ($2p^3\,^4S+2p^2 3s\,^4P$)←($2p^3\,^4S+2p^3\,^4S$) would lie in the Schumann region at λ850. Herzberg[19] has shown that it is the A′-state which is formed of one neutral unexcited ^4S atom and one neutral ionised ^3P atom while the ground state is formed of ^2D atom and ^3P ion of N. Thus to get the value of the ionisation potential of N_2 we have to subtract 3·156 volts, the excitation potential of A′-state, which makes it 18·67−3·156 =15·51 volts.

6. First Positive Group of Nitrogen

From the earliest times of Band-Spectroscopy, the first positive group of nitrogen has been the subject of investigation by a large number of observers. The reason lies in the fact that these bands have a prominent character in the most easily accessible region of spectrum and show a marked regularity. The visible part of this group was investigated by Deslandres[20] and Von der Helm[21] under low dispersion and by Birge[22] under high dispersion in the second order of twenty-one feet grating. Fowler and Strutt[23] found that some of the bands of this group were intensified while others were either very faint or entirely absent in the after-glow of active nitrogen. They designated them as the α-bands. Other changed conditions of excitation such as temperature also altered their appearance. Angerer[24] made an exhaustive study of these bands and found that at low temperature the band heads are far more intense relative to the rest of the bands than at ordinary temperature.

The tempting regularity of these bands at the red end is particularly inviting. Birge[22] measured the most conspicuous lines and groups of lines with a constant deviation spectrograph between λ 6800—λ 7650. Croze[25] using a prism spectrograph measured 10 other bands in this region. Pfund[26] and Poetker[27] using a powerful source of illumination extended the search of the new members of the group in the infra-red. The latter employed photographic plate as well as a three-junction compensating vacuum thermopile as the detector.

In an earlier investigation Birge made the vibrational analysis of these bands and gave the following formula for the band heads:—

$$\nu_{head} = 9518{\cdot}6 + (1718{\cdot}40\, v' - 14{\cdot}437\, v'^2) - (1446{\cdot}46\, v'' - 13{\cdot}929\, v''^2) \quad . \quad . \quad . \quad . \quad (9)$$

However, his assignment of the vibrational quantum numbers was slightly modified by Poetker[27] who found that a slight alteration was 'the only way of reconciling several flaws in what was otherwise a perfect agreement between theory and experiment, prediction and observation.' This change involved in diminishing Δv by unity in the observed sequences. The band head λ9108 observed by Croze[25] was designated as (0, 0) band by Birge[22] but Pfund[26] found that the band head at 1·042 μ was most intense of all the observed bands.

Soon after the attempts regarding the vibrational analysis of these bands Naudé[28] made a rotational analysis and subsequently[29] gave a more complete work on some of the less developed bands for in their structure the overlapping was considerably less. As usual he

employed, as the source of light, an inverted Π-shaped and water cooled discharge tube which was capable of carrying a current of 1·6 amps. The spectrum was photographed end-on on the 21 ft. Rowland grating of the Chicago University, which gave a dispersion of ·7A° per mm. in the third order and 1·3 A° per mm. in the second order. He measured the bands (4, 1) λ 6788 ; (5, 2) λ 6705; (6, 3) λ 6623; (3, 1) λ 6127; (6, 2) λ 6070 ; (7, 3) λ 6013 against Neon standards. The comparison spectrum was taken by passing a discharge through Neon which was circulated in the same tube and later recovered in a liquid air trap. A complete rotational analysis was only made of (5, 2) and (6, 3) bands.

For a long time the upper and lower levels which participate in the emission of the first positive group were called B and A levels. As is well known these bands are degraded towards the violet. From the analysis of the second positive group of bands it was completely established that the upper level B was $^3\Pi$, while the lower level A in all probability was thought to be either $^3\Sigma$ or $^3\Delta$. Naudé's analysis favours the view that they are due to $^3\Pi-{}^3\Sigma$ transition.

It is interesting to note that what appeared to be three strong and one weak components of the individual bands in a spectrogram of low dispersion came out to be in reality three groups of three strong branches which gave P_1, Q_1, R_1, P_2, Q_2, R_2, P_3, Q_3, R_3, *i.e.*, nine branches in all. They result from the molecular multiplet $^3\Pi_{2,1,0}$ and conform to the transitions $^3\Pi_2-{}^3\Sigma$, $^3\Pi_1-{}^3\Sigma$ and $^3\Pi_0-{}^3\Sigma$. Further, the rotational level in each set are again double due to Λ-type doubling.

As in the case of Lyman bands so in the present group the branches show alternating intensity approximately in the ratio 2 : 1. If i is the nuclear moment the ratio of intensity is given by

$$\frac{i+1}{i} = \frac{2}{1} \quad \text{or} \quad i = 1 \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This establishes finally that the nuclear magnetic moment of nitrogen is unity.

Naudé gave the following values of the rotational constants for the two levels B and A :—

Level A

$B_{e''} = 1{\cdot}440 \text{ cm}^{-1}$ $\qquad D_{e''} = -5{\cdot}5\times10^{-6} \text{ cm}^{-1}$

$\alpha_{e''} = 0{\cdot}013 \text{ cm}^{-1}$ $\qquad r_{e''} = 1{\cdot}289\times10^{-8}$ cm.

Level B

$B_{e'} = 1{\cdot}66 \text{ cm}^{-1}$ $\qquad D_{e'} = -6{\cdot}2\times10^{-6} \text{ cm}^{-1}$

$\alpha_{e'} = 0{\cdot}023 \text{ cm}^{-1}$ $\qquad r_{e'} = 1{\cdot}20\times10^{-8}$ cm.

It may be recalled here that some of the bands of the first positive group of nitrogen appear in the aurora, active nitrogen, night sky, planetary absorption, and the luminescence of the solid nitrogen when bombarded with cathode or canal rays. The brilliant luminescence spectrum was studied in some detail by Vegard[30,31] at the Cryogenic Laboratory at Leyden and McLennan[32,33,34] and his collaborators at Toronto. Recently Kaplan[35] has tried to identify a large number of luminescence bands N_1, N_2, N_3, N_4 and others with the bands of the first positive group. We will refer to the luminescence bands frequently in connection with the second and fourth positive group of nitrogen, etc., and therefore a table of these bands is given below.

Table 7.—Luminescence Bands of Solid Nitrogen.

2347	2781	3055	3285	3732	4585	5552		6187
2479	2903	3105	3388	3980	4775	5616	N_1	6400N_3
2623	2961	3158	3502	4255	5230N_2	5659		6725
2765	3009	3234	3644	4493		5945N_4		8535

The above table is due to McLennan, Ireton and Samson.[34] It will be more convenient to give Kaplan's identification in a tabular form.

Table 8.—Comparison of the First Positive and the Luminescence Bands.

Luminescence Bands	Designation	Transition	1st Positive Bands	REMARKS.
5552 5616 5659	N_1	$B_{16} - A_{12}$ $B_{15} - A_{11}$ $B_{14} - A_{10}$	5565 5617 5665	λ 5552 corresponds to the second head of λ5565 (1st+*ve*). Bands are not obtained in Aurora and are single-headed.
5204·2 to 5240 components are:— (1) 5204·4 (2) 5210·4 (3) 5214·3 (4) 5220·1 (5) 5224·4 (6) 5228·8 (7) 5235·0 (8) 5240·0	N_2	$B_{17} - A_{12}$ $B_{16} - A_{11}$	5207 5240	λ 5207—λ 5240 (1st+*ve*) include all the heads eight components in the luminescence. In the Aurora their wavelengths are (1) 5207, (2) 5200, (3) 5228, (4) 5235, (5) 5166, (6) 5230, etc.
6360 to 6500 Max at 6400	N_3	...	6465	

Luminescence Bands	Designation	Transition	1st Positive Bands	REMARKS.
		$B_9 - A_6$	6394	Observed in Active Nitrogen together with 6469, 6545.
		$B_{10} - A_7$	6323	Observed both in Aurora and Night sky.
5945	N_4	$B_8 - A_4$	5959	Observed in Aurora corrs. to 2nd component of λ5959.
5939	Components.	..	...	Observed in Aurora corrs. to 3rd component of λ5959.
5932		...	..	Observed in Aurora corrs. to 4th component of λ5959.
6187	...	$B_4 - A_0$ or $B_{12} - A_9$	6187 6185	Obtained in planetary absorption.
8535	...	$B_3 - A_2$	8541	
6725	...	$B_5 - A_2$	6704	6704
7270	...	$B_6 - A_4$	7273	Observed in planetary absorption and night sky.
5945	...	$B_8 - A_4$	5959	Third and fourth heads of λ5959 make up λ5945 and the second head is observed in Aurora.

The above correlation seems to be best in the face of the limited data at our disposal and it is desirable to continue further work on these lines to completely understand this interesting phenomenon.

7. The Second Positive Group

The second positive group of nitrogen is memorable on account of the fact that it was the first band whose vibrational analysis was first done by H. Deslandres[36] and gave rise to his classical formula and diagram about the progressions. It has since been the subject of investigation by an innumerable number of investigators. These prominent bands lying in the region λ 5438 – λ 2692 are designated the second positive group of bands and are degraded towards the violet. They result from the transition between two levels C and B which according to the modern notation are $^3\Pi_u$ and $^3\Pi_g$ respectively.

Like the first positive group of nitrogen this group was also observed at an early stage of Band-Spectroscopy when Lecoq,[37] Hasselberg,[38] Deslandres[36] and others described the results of their observations on such prominent groups of bands. A brief summary of such earlier attempts can be found in Kayser's *Handbuch der Spectroscopy Band,*

5, 1910. It was Mecke and Lindau[39] who made a fuller vibrational analysis of these bands in the form of the well-known Deslandres band-head scheme. Through several years of most elaborate work such a table has undergone necessary modifications and the reader is referred to Table 1 of the recent paper by Büttenbender and Herzberg[45].

Attempts on the rotational analysis of these bands were initiated eleven years ago by Hulthen and Johansson[40,41] who made the rotational analysis of a large number of bands, namely, (0, 0), (0, 1), (0, 2) and (1, 3). Immediately after the publication of their results Lindau[42] gave the rotational analysis of (0, 1), (0, 2), (0, 3), (1, 2), (1, 3), (1, 4), (2, 4) and (2, 5). However, their observations were far from being complete and in subsequent years we find several papers in which rotational analysis of different bands is described by several investigators.

Coster, Brons and Van der Ziel[43] photographed the spectrum from the usual Π-shaped tube in the second and fourth orders of a large grating in the region between λ 3600 to λ 2900 and made the rotational analysis of (0, 0), (1, 0), (2, 3), (3, 3), (4, 2) and (4, 4) bands. They found that the Π-levels are triple with $\Omega = 2, 1, 0$. Like Naudé[29] they find for smaller J-values that the $^3\Pi$-level corresponds to Hund's coupling case a and for larger J-values to the case b. In the case a the selection rule $\Delta\Sigma = 0$ permits only the transitions $^3\Pi_2 - {}^3\Pi_2$, $^3\Pi_1 - {}^3\Pi_1$, $^3\Pi_0 - {}^3\Pi_0$. It is worthy of note that only the P- and R-branches are very bright while Q-branch is invisibly faint. They have obtained the values of the rotational constants B'_v and B''_v for the levels involved in their analysis; for $v = 0$ the B-values are given below

$$B_0' = 1{\cdot}816 \text{ cm}^{-1} \quad B_0'' = 1{\cdot}623 \text{ cm}^{-1}.$$

They have given the following slightly modified null-line formula

$$\nu = 29670{\cdot}6 + (2020{\cdot}00v' - 26{\cdot}40v'^2 + 1{\cdot}158v'^3 - 0{\cdot}5542v'^4) - (1719{\cdot}64v'' - 14{\cdot}47v''^2). \quad . \quad . \quad . \quad . \quad (11)$$

They find also that the predissociation limit lies 38770 cm^{-1} above the $^3\Pi_1$ level of the lover state B.

Guntsch[44] has again made the rotational analysis of some of the bands of the second positive group in the third order of a concave grating where the dispersion is ·65A° per mm. The values of the rotational constants obtained by him are as follows

$$B_0' = 1{\cdot}813 \text{ cm}^{-1} \quad B_0'' = 1{\cdot}625 \text{ cm}^{-1}$$

The most interesting point to note in this connection is that Guntsch has observed a Q-branch as well in some of the bands which failed to appear in the plates of his predecessors.

Probably the most comprehensive work on the rotational structure of the second positive group is due to Büttenbender and Herzberg[45] who made their analysis on the six meter concave grating at Tübingen in the second order with a dispersion of 1·5A°. per mm. They gave the value of the rotational constants with the great accuracy of $\pm$ ·0005cm^{-1}, studied the structure of hitherto undetermined bands which are included in (2,0), (3,0), (3,1), (3,5) (4,1) (4,2) and (4,6) bands, completed the work of Lindau on the (2, 4) band and studied in detail with the aid of microphotograms the phenomenon of predissociation in some of these bands. The accuracy permitted in the measurement of the lines was $\pm$ 0·1cm^{-1}. They observed three intense R as well as P branches while the Q-branch was not found to be present at all due to its faintness Further, only with the (3, 5) band a Λ-type doubling was observed for the transition $^3\Pi_0 - {^3\Pi_0}$. The rotational term was found to be of the form

$$F_1(J) = B(J+\tfrac{1}{2})^2 - D(J+\tfrac{1}{2})^4 - \varepsilon(J+\tfrac{1}{2}) \qquad . \quad . \quad . \quad (12)$$

On account of the high precision of the measurement claimed by Büttenbender and Herzberg we give below a complete list of the rotational constants obtained from their analysis.

Table 9.—Rotational constants of levels C and B of Nitrogen.

Quantity	C $^3\Pi_u$	Quantity	B $^3\Pi_g$
B_e'	1·8309 cm^{-1}	B_e''	1·6430 cm^{-1}
B_0'	1·8212 cm^{-1}	B_0''	1·6342 cm^{-1}
α_e'	0·0185 cm^{-1}	α_e''	0·0176 cm^{-1}
α_0'	0·0200 cm^{-1}	α_0''	0·0177 cm^{-1}
$\gamma_e'=\gamma_0'$	$-$0·0015 cm^{-1}	$\gamma_e''=\gamma_0''$	$-$0·0001 cm^{-1}
D_e'	0·64$\times$10 cm^{-1}	D_e''	0·63$\times$10 cm^{-1}
$\beta_e'=\beta_0'$	+0·030$\times$10^{-5} cm^{-1}	$\beta_e''=\beta_0''$	+0·013$\times$10^{-5} cm^{-1}
D_0'	0·66$\times$10^{-5} cm^{-1}	D_0''	0·64$\times$10^{-5} cm^{-1}
ε'	$-$0·30 cm^{-1}	ε''	$-$0·30 cm^{-1}
I_e'	15·107$\times$10^{-40}g cm^2	I_e''	16·835$\times$10^{-40} g cm^2
I_0'	15·187$\times$10^{-40}g cm^2	I_0''	16·926$\times$10^{-40} g cm^2
γ_e'	1·1438 A°U	γ_e''	1·2074 A°U
γ_0'	1·1468 A°U	γ_0''	1·2107 A°U

As the principal object of their paper is to determine precisely the predissociation phenomenon we give below the predissociation limit as obtained by them above the ground state $^1\Sigma_g^+$

$$E_{\text{pred}} = 97960 \pm 40 \text{ cm}^{-1}$$

which is found to correspond to the dissociation into two ^{2}D atoms of nitrogen.

It may not be out of place to mention here the fact that the second positive bands are not obtained with v'-values greater than 4. Herzberg and Kaplan[46] pointed out that $v'=4$ is only 13·9 volts which corresponds to the dissociation of the molecule into two ^{2}D metastable nitrogen atoms which is equivalent to the predissociation of the molecule. As mentioned above Büttenbender and Herzberg's[45] recent analysis lends support to this view. However, Kaplan has discussed the possibility of obtaining the second positive bands with higher v'-values and such bands have actually been obtained in the luminescence of solid nitrogen. In Table 7 we have already given a list of all the luminescence bands as obtained by McLennan, Ireton and Samson.[34]

Kaplan[35] identified the band λ2961 of the luminescence with the band (3,1) λ2962 in the second positive group. Similarly, the bands λ3105, λ3158, λ3285, λ3502, λ3644, and λ4490 observed in luminescence may correspond to λ3104, λ3159, λ3285, λ3500, λ3644, and λ4490 of the group under consideration. While the bands λ2479, λ2623, λ2765 correspond with (6, 0) λ2479, (7, 2) λ2621, (9, 4) λ2761 of the calculated second positive bands. In the calculation of the position of these bands Kaplan used the following formula for the C-level.

$$E = 2018{\cdot}67v' - 26{\cdot}047v'^2 + 0{\cdot}9873v'^3 - 0{\cdot}546v'^4 \quad . \; . \; . \; . \; . \quad (13)$$

Recently Kaplan[47] has reported new members of this group with higher v'-values in a special discharge tube. We give below a table of bands observed by him together with their calculated positions.

Table 10.—Observed second positive bands in Luminescence and their calculated wavelengths.

Obs	4747	4737	...	4732	4453	4440	4435	4190
Cal	...	...	...	(8,14) 4719	...	(8,13) 4441	...	(8,12) 4189
Obs	4180	4174	3180	3164	3027	3010	2886	2863
Cal	...	...	(9, 7) 3171	(7, 6) 3150	(9, 6) 3025	(7, 5) 3002	(9, 5) 2888	(7, 4) 2866

It will be remembered that these bands show an alternation in intensity of their branches which is so characteristic of the N_2-molecule. Curiously enough the higher v-value bands degrade towards the red instead of violet. The reason is not far to seek. This is due to the extremely rapid convergence of the vibrational levels of $C\,^3\Pi$-state.

In the latest report in the *Physical Review* Kaplan[48] points out that three strong bands λ4732, λ4435, λ4174 correspond to a new system (v', 12), (v', 11) and (v', 0). The observation of such bands in a discharge tube and the luminescence of solid nitrogen suggests that under special circumstances vibration levels higher than $v'=4$ can participate in the emission of the bands of this group, but more work has to be done on these lines.

The third positive group.—In addition to these bands another set known as the third positive bands was obtained in nitrogen discharge. It was noticed early that a slight trace of oxygen was necessary for the production of these bands. But now it has been definitely, proved to be due to NO, hence no description of these bands is included here.

8. The Fourth Positive Group

This group of nitrogen bands results from a transition from the so far highest known level D to the level B. The excitation of the molecule to the state D, so that it may emit the fourth positive bands, requires a very large expenditure of energy. This was the reason why this characteristic group failed to appear in the earlier observations of Deslandres and others in the ordinary discharge tubes

Strutt and Fowler[49] for the first time observed that in the condensed discharge spectrum of nitrogen the first positive group diminished in intensity while the second positive group increased and in addition a new series of seven five-headed bands appeared. In conformity to Deslandres' notation, these bands were named as the "Fourth Positive Group." They definitely proved that these were due to nitrogen and found, with the aid of a high dispersion spectrograph that out of the five heads of a single band, the most refrangible was the strongest of all in brightness.

Later Strutt and Kaplan[50] observed that, under certain special conditions, these bands may be obtained in an uncondensed discharge as well. Thus Kaplan found that this group was well developed if a mild discharge was passed through Active Nitrogen He argued that in the Active Nitrogen are present nitrogen molecules in the metastable state (A) and a mild discharge raises some of these molecules to the higher state D. The difference of energy between the levels D and A is about

6·8 volts and the evidence cited in favour of the above view is strengthened according to Kaplan by the fact that electrons of as low as 6·8 volts energy in Active Nitrogen are able to excite these bands.

Sponer[51] suggested that all the seven individual bands of this group originate from the D-level with $v'=0$, so that the vibrational scheme may be represented as follows :—

Table 11.—Fourth positive bands (A°. U)

v' \ v''	0	1	2	3	4	5	6
	2260·8	2351·4	2448·0	2550·7	2660·5	2777·9	2903·9
	59·6	50·3	47·0	49·7	59·3	76·5	02·0
0	58·4	49·0	45·6	48·4	57·9	75·1	00·3
	57·1	47·5	44·0	46·6	55·8	72·8	2898·1
	56	46·4	42·8	45·3	54·5	71·4	96·6

The (0, 0) band located at λ2260·8 requires 14·8 volts for its excitation and formula for ν_{head} is

$$\nu_{head}=44218-(1718{\cdot}40\ v''-14{\cdot}437\ v''^2)\ . \quad . \quad . \quad . \quad (14)$$

It may be mentioned here that $f(v')$ for this group is identical with $f(v')$ of the first positive and $f(v'')$ of the second positive group of bands. (*Vide* equations 9 and 11.) This quantum vibrational analysis therefore confirms the view held by Fowler and Strutt[49] before the advent of the quantum theory that at least one level is common in the production of the first, second and fourth groups. In fact, it is not far to see that the level B $^3\Pi_g$ is a common level. These facts can be very well seen from the vibrational energy diagram of these three groups given to scale by Birge for the first time.

As remarked earlier only some of these bands appear in Luminescence spectrum of solid nitrogen but not all. Kaplan[35] identified some of these bands. The luminescence bands 2347, 2781 and 2903 agree well with the heads 2347·5 or 2346·4, 2777·9 and 2903·9 or 2902 of the fourth positive bands. This group of bands is not very well analysed and a complete rotational analysis may reveal many interesting points and we have to wait till such work is completed.

9. The Vegard-Kaplan Intercombination System

As mentioned in the §3 two system of levels denoted by the small letters (singlets) and capital letters (triplets) for a long time remained unconnected like the Helium singlets and triplets, and ultimately the connection was established through the work of Vegard.[52] It arose out of his attempt to prove that some of the auroral lines were due to the brilliant luminescence produced in solid nitrogen in the upper atmosphere by bombardment of high speed electrons. In pursuance of this idea, while he was carrying out experiments in the laboratory on luminescence produced by the bombardment of solid nitrogen by high speed electrons, Vegard for the first time obtained in emission the long sought intercombination system. He got a system of new bands in the luminescence spectrum of mixtures of solid Argon and Nitrogen. He designated it provisionally as the ε-system. The bands which were obtained on the plates of Vegard were found to be multiple-headed. He attributed them to a $A^3\Sigma - X^1\Sigma$ transition on the basis of rather uncertain evidence.

Kaplan,[4] later on, obtained a set of single-headed bands in the spectrum of gaseous nitrogen produced in a special form of discharge tube[53, 54] in which the after-glow was present. A comparison with the strong heads of Vegard's ε-system showed that these bands[55] were identical with those of Vegard. It may be mentioned in this connection that only that part of the tube in which the after-glow was prominent gave these bands. Although the nature of discharge varied with the current and gas-pressure inside the tube, yet the presence of these bands was found to depend only on the after-glow. However, lower pressures inside the discharge tube made these bands stronger so that they could be photographed on an instrument of high dispersion. Further, low pressure discharge seemed to help in the development of the rotational structures of these bands. Recently Kaplan [56, 57] found that at very small currents, *i.e.*, the green stage of the discharge λ2760 (0, 6); λ2603.8 (0, 5) members of this group appeared together with higher members of the second and first positive groups. On further decreasing the current greatly the negative bands disappeared and the intensity of Vegard-Kaplan bands enhanced considerably.[58]

The number of bands of this system as obtained by Kaplan was much less than in the so-called ε-system. Kaplan[55, 59] tried to give a vibrational analysis of the system and at first found that the band-system may be due to the transition between a new level probably $^3\Sigma$ of two ^4S

nitrogen atoms and the well known ground state level, namely, $A^1\Sigma$. His analysis was different from that of Vegard inasmuch as v''-values in Vegard's scheme were higher by unity from those of Kaplan. The lower state vibrational energy differences were identical with those of $A^1\Sigma$ level as obtained from Lyman bands, but regarding the upper state great uncertainty prevailed. As mentioned above, Kaplan asserted at this stage, on the basis of the heat of dissociation, that the upper level was really $^3\Sigma$ of two ^4S atoms. Later, Hopfield[60] showed that the formula for the band heads of this system as given by Vegard and Kaplan were widely different from a formula given by him. He gave the following formula for the band heads

$$\nu = 49774{\cdot}4 + (1446{\cdot}46v' - 13{\cdot}93v'^2) - (2345{\cdot}16v'' - 14{\cdot}445v''^2). \quad \ldots \quad (15)$$

It has been later confirmed that this formula for the intercombination bands is correct.

A comparison of the above equation with (1) and (9) for the Lyman bands and the First Positive bands shows clearly that the upper level of this Vegard-Kaplan System is really $^3\Sigma$ (A) and the lower level is $^1\Sigma_g^+$ (X). Thus it was convincingly proved that this new group was really the hitherto undiscovered intercombination system. The difficulty of obtaining these bands sufficiently developed for a suitable rotational analysis is very great and a complete work on these lines is yet in its infancy.

Recently Cabannes and Dufay[61] obtained a large number of bands in the night sky which were identified as members of the Vegard-Kaplan intercombination system with higher v'- and v''- values. They found that some of these bands (2, 14) (3, 14) were very intense. This is to be expected, according to the Franck-Condon principle, because there is a large difference between r_0-values of the potential energy curves of the two states as shown in the Fig. 2. There are three very important points which deserve mention at this stage:

Firstly, for a reliable identification of these bands in the night sky and other terrestrial sources the wavelengths of these intercombination bands should be very accurately measured, say, to the third place of decimal. The accurate measurements can be profitably performed with instruments of great precision from the sources of illumination obtainable in a laboratory. It is now not difficult to obtain these bands with great intensity under suitable conditions of discharge and therefore instruments of high dispersion as well can be employed. These accurate measurements will help considerably in explaining the conditions of excitation of the spectra of Aurora and night sky.

Secondly, the sunlight has to pass through a length of nitrogen gas which is nearly 6 kilometres in length under N. T. P. (height of the homogeneous atmosphere for nitrogen only). As the Vegard-Kaplan bands are due to the transition from the excited level A to X, the normal level, these bands are expected to appear in absorption as telluric lines. There are lot of unidentified lines in the region λ5000-3000, but we cannot be sure of their identification before the Vegard-Kaplan bands are accurately measured in the laboratory.

Thirdly, we may expect that Vegard-Kaplan bands should also be obtained in absorption in the laboratory but the length of the absorption column would be very long. The absorption of these lines in solar spectrum is due to 6 kilometres of nitrogen at N. T. P. If we obtain nitrogen gas in a cylinder 30 metres long at a pressure of 200 atmospheres then we can hope to duplicate the propagation of solar light through our atmosphere but such experiments are very difficult to carry out. We may mention in this connection that to obtain the absorption of atmospheric bands of oxygen in the laboratory, King[62] had to use 7 metres of oxygen for the A-band and approximately 40 metres for the B-band at ordinary pressures. Recently Frost and Oldenberg[63] were unsuccessful in obtaining absorption spectrum of metastable nitrogen molecule under best experimental conditions.

10. New Band Systems of Nitrogen

A. Van der Ziel[68] has reported the presence of 14 bands which apparently belong to a new band-system of nitrogen and lie in the region λ 2000 – λ 2800 A°.U. These bands were obtained by him from a source of illumination which consisted of a Π-tube of Pyrex glass and contained nitrogen at low pressure and run at a high current density of 10 amp / cm². The transition giving rise to these bands may either be ${}^{1,3}\Sigma_u^+ \rightarrow {}^{1,3}\Sigma_g^+$ or ${}^{1,3}\Sigma_g^- \rightarrow {}^{1,3}\Sigma_u^-$. The upper and lower levels were not found to correspond with any known level of nitrogen. The lower state was stabler of the two and the formula for the vibrational levels of this state was found to be

$$E_v = 1516{\cdot}2\, v - 11{\cdot}55\, v^2 \qquad (16)$$

He made the rotational analysis of (0, 0) (0, 4) and (0, 5) bands of this system and obtained the following rotational constants

$$B_0' = 1{\cdot}72 \text{ cm}^{-1} \text{ and } B_0'' = 1{\cdot}47 \text{ cm}^{-1}.$$

At present the excitation potentials of these two levels are not known and further work is required to give tangible information about this new system.

Recently Kaplan[48,64] has obtained in his discharge tube quite a large number of new bands which can be apparently classified into a large number of groups. They are so numerous that only a detailed analysis can reveal the true nature of their complexity. Till now no satisfactory analysis has been done and it appears that even in their vibrational analysis and the assignment of levels partaking in transitions, due to which they originate, the ground is constantly shifting. We, therefore, propose to give a brief description of these band-systems of nitrogen and hope that in a short time we will be in possession of many interesting details due to the labours of those who are actively engaged in revealing the mysteries of the nitrogen molecule.

Kaplan[48] obtained at first bands whose heads were at λ 2153, 2225, 2301 and 2381. At low pressure these bands were intensified. Subsequently he obtained two more bands of the same system at λ 2288, 2366. He designated them as (0, 0), (0, 1), (0, 2), (0, 3), (1, 3) and (1, 4) bands respectively. The frequency differences of the lower vibrational levels correspond very closely to the frequency differences between the lower vibrational levels of Van der Ziel's[65] system. They may be the members of the Hopfield-Rydberg series which we have described in the foregoing pages.

A second system in the same region consists of bands which are 2740 (0, 3), 2365 (0, 2), 2536 (0, 1), 2720 (1, 4), 2620 (1, 3), 2522 (1, 2), 2432 (1,1), 2421 (2, 2) and 2510 (2, 3). The last two bands are rather faint while the first three were obtained in earlier observations of Kaplan.

Kaplan announced at the Berkeley meeting of the American Physical Society that the five bands 4732, 4435, 4174, 3010 and 2864 were the members of the second positive group originating from higher vibrational states. But a later analysis showed that the first three bands are $(v', 12)$ $(v', 11)$ and $(v', 0)$ members of a new system and the two ultra-violet bands are (0, 1) and (0, 0) members of yet another system. It is believed that the lower electronic level for these bands is $B^3\Pi$-state of N_2-molecule. Further investigations on these bands as well are in progress.

Besides the bands which have been tentatively classified as described above there are no less than forty bands[64] which do not seem to belong to any known group of bands of nitrogen. However, it is clear from their general characteristics that they are members of several new systems which remain yet undiscovered in this complex molecule.

11. Molecular Spectrum of N_2^+

We will now briefly summarise the molecular spectrum of N_2^+ to complete the spectroscopic account of the nitrogen molecule. At present four electronic levels of N_2-molecule are known which have been denoted by $X'^2\Sigma_g^+$, $A'^2\Sigma_u^+$, $B'^2\Sigma_u^+$ and $^2\Pi_u$ respectively. (See Fig. 1). The last electronic level is known only from the perturbations which it causes in the level $A'^2\Sigma_u^+$. No band system of N_2^+ is known for which $^2\Pi_u$ is the initial or the final state. From the knowledge of perturbations it was located ·65 volts above the ground level $X'^2\Sigma_g^+$ of N_2^+. It is therefore thought that on account of its closeness to the ground level the allowed transition $^2\Pi_u \rightarrow X'^2\Sigma_g^+$ lies beyond the region of observation and the other transitions $B'^2\Sigma_u \rightarrow {}^2\Pi_u$ and $A'^2\Sigma_u^+ \rightarrow {}^2\Pi_u$ are forbidden. This fact explains why no band system in which the level $^2\Pi_u$ partakes is observed.

The transition $A'^2\Sigma_u^+ \rightarrow X'^2\Sigma_g^+$ gives rise to the negative bands. The negative bands of nitrogen are quite well known and were described by Deslandres,[93] Rayleigh,[94] Frierich,[95] Lindau[96] and Mecke.[89] Fassbender[97] first made extensive rotational analysis of some of the bands and Herzberg[19] observed many new bands. Then Coster and Brons[98] made a further rotational analysis of (0, 0), (0, 1), (1, 2), (2, 3), (0, 2), (1, 3), (2, 4), (3, 5), (4, 6), (10, 9), (8, 6), (10, 8) bands and gave the following null line formula

$$\nu = 25566{\cdot}0 + 2396{\cdot}22\,v' - 24{\cdot}070\,v'^2 - 0{\cdot}6365\,v'^3 - 0{\cdot}04949\,v'^4$$
$$-(2191{\cdot}02v'' - 19{\cdot}196\,v''^2 - 0{\cdot}0400\,v''^3) \quad . \quad . \quad . \quad (17)$$

In a special type of source Childs[99] was able to excite much higher rotational states of these bands and observed a large number of hitherto unknown perturbations in the (0,0) and (0,1) bands. Recently Crawford[100] and Tsai have made the rotational analysis and a study of perturbations in the bands (2, 2), (3, 4), (3, 5), (5, 7), (6, 8), (0, 3), (1, 4), (2, 5).

Another known transition of the ionised molecule is $B'^2\Sigma_u'^+ \rightarrow X'^2\Sigma_g^+$. This gives rise to Hopfield-Watson-Koontz bands. Hopfield observed a few bands in the region $\lambda\,1721-\lambda 2054$ which were degraded towards the red. They were obtained in a mixture of helium and nitrogen gas in emission only. Watson and Koontz obtained quite a large number of bands with higher v'- and v''- values in a condensed discharge through Tank Helium. They gave the following null-line formula for the bands.

$$\nu = 54024 + 2173{\cdot}2\,(v'+\tfrac{1}{2}) - 10{\cdot}43\,(v'+\tfrac{1}{2})^2 - 0{\cdot}017\,(v'+\tfrac{1}{2})^3$$
$$-2207{\cdot}16\,(v''+\tfrac{1}{2}) + 16{\cdot}136\,(v''+\tfrac{1}{2})^2 + 0{\cdot}0400\,(v''+\tfrac{1}{2})^3. \qquad (18)$$

H. H. Brons[101] fixes the heat of dissociation of the X′-state to be 6·3 volts and this assumption leads to the result that the three electronic states $^2\Sigma_g^+$, $^2\Pi_u$, $^2\Sigma_u^+$ all dissociate into the same products ^3P (N^+) and ^4S (N). This result is quite contradictory to the results of Herzberg. We have, however, found Herzberg's idea more in agreement with certain spectroscopic facts mentioned in the present paper.

12. Heat of Dissociation of Nitrogen

The correct numerical value of the heat of dissociation of nitrogen, *i.e.*, the energy required to separate the normal molecule into two unexcited atoms has long been in dispute. Different methods of attack have been adopted from time to time by various investigators of which following are examples: thermochemical methods, Active Nitrogen experiments, sensitised fluorescence, absorption spectra, Birge and Sponer's extrapolation of vibrational levels, excitation of N_2^+ bands, electron bombardment and predissociation. The values obtained by different methods are so divergent amongst themselves that no reliance could rightly be placed on any one of them. The matter appears to have been cleared up recently by Herzberg and Sponer[66] who find that the most probable value of the heat of dissociation of nitrogen is **7·34 ± 0·02** volts.

Herzberg and Sponer arrived at this result from a careful discussion of the predissociation phenomena observed in the various emission bands of nitrogen by the authors mentioned in the last column of Table 12, which contains an accurate description of the results so far obtained. The predissociation limit for the second positive band was first observed by Coster, Brons and Van der Ziel at 38770 cm^{-1} = 4·78 volts, above the electronic level $B\,^3\Pi_g$ of nitrogen. At the time of their observations, the difference between $A\,^3\Sigma_u^+$ and $X\,^1\Sigma_g^+$ levels was not accurately known. However, we know now from the Vegard-Kaplan intercombination system that $A\,^3\Sigma_u^+$ level is 6·14 volts above the $X\,^1\Sigma_g^+$ level and $B\,^3\Pi_g$ level is 1·17 volts above the level $A\,^3\Sigma_u^+$, so that the energy value of $B\,^3\Pi_g$ state is 6·14 + 1·17 = 7·31 volts above the ground state. Thus the limit of predissociation as obtained by Coster and his collaborators is now fixed at 4·78 + 7·31 = 12·09 volts above the ground level X. Practically the same value was obtained by Büttenbender and Herzberg who took great care in their measurements and studied photometrically the predissociation in (4, 1), (3, 1), (2, 0), (3, 0) and (4, 2) bands.

They fixed the limit of predissociation at 12·07 volts for the second positive band.

Table 12.—Heat of Dissociation of Nitrogen.

Band	Type of predissociation	Energy-value of the limit	Products of Dissociation	D_{N_2}	Author
II Positive Group	Rotation at v'= 4, 3, 2, 1 and J'=28, 43, 55 and 65 respectively.	12·07 volts	$^2D+^2D$	7·347 ± 0·005 volts	Coster, Brons and Van der Ziel[43] Büttenbender and Herzberg[45]
I Positive Group.	Rotation, v'=12, J'=32, 33 and 35 for $^3\Pi_2$, $^3\Pi_1$, $^3\Pi_0$.	9·79	$^4S+^2D$	7·32 volts	Kaplan[69, 70] and Van der Ziel[67, 68]
Lyman-Birge-Hopfield Bands.	Vibration at v'=9	10·24	$^4S+^2D$	7·9 volts	Watson and* Koontz[71]

In the case of the first positive group ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$) Kaplan[70] first observed the predissociation phenomena in (13, 9), (14, 10), (15, 11), (14, 9) and (15, 10) bands. A. Van der Ziel made a detailed investigation of the (12, 8) band of this group. He observed a sudden decrease in the intensity of the lines at J=32, 33 and 35 for $^3\Pi_2$, $^3\Pi_1$ and $^3\Pi_0$ levels respectively. From these results he definitely concludes that products of dissociation corresponding to the limit of predissociation are ^4S and ^2D atoms of nitrogen for the first positive band. The predissociation limit in this case lies at 9.79 volts.

Herzberg and Sponer observed that the energy difference between the two predissociation limits is 12·07 − 9·79 = 2·28 volts, and they remembered that the only energy level difference in the nitrogen atom with which the above figure agrees is $2p^3$ ($^4S - ^2D$) of nitrogen. From this they concluded that for the products of dissociation in the two cases we have N $2p^3$ ^4S and $2p^3$ ^2D in corresponding positions. We may assume that

$$N_2 + 12{\cdot}07 = N(^2D) + N(^2D) \quad \text{[Predissociation in the second positive bands.]} \quad . \;.\;. \quad (19)$$

* In a private letter, Prof. Watson informs us that he is not quite sure of this value now.

$N_2 + 9{\cdot}79 = N(^4S) + N\ (^2D)$ [Predissociation in the first positive bands]. . . . (20)

This enables us to calculate the heat of dissociation D_{N_2} of N_2 into two N (^{4}S) atoms of nitrogen. We have

$$N_2 + D_{N_2} = N\,(^4S) + N\,(^4S). \quad \ldots\ldots \quad (21)$$

Comparing (21) with (20) and (19) we obtain

$$D_{N_2} = 9{\cdot}79 - \{N\,(^4S) - N\,(^2D)\} = 7{\cdot}42 \text{ volts}$$

and $$D_{N_2} = 12{\cdot}07 - 2\,\{N\,(^4S) - N\,(^2D)\} = 7{\cdot}33 \text{ volts.}$$

Table 13.—Excitation Potentials and Products of Dissociation of Nitrogen levels

Terms	Notation	Excitation energy in volts	D. volts	Dissociation Products
X.	$^1\Sigma_g^+$	...	7·34	$^4S+^4S$
A	$^3\Sigma$	6·14	3·56	$^4S+^2D$
B	$^3\Pi$	7·32	4·76	$^2D+^2D$
a	$^1\Pi$	8·51	5·7	$^2D+^4S$
C	$^3\Pi$	10·98	1·10	$^2D+^2P$
D	$^3\Sigma$	12·77	...	$^2D+^2P$
X′	$^2\Sigma_g$	15·52	6·31	$^2D+^3P$
A′	$^2\Sigma_u$	18·67	3·7	$^4S+^3P$
B′	$^2\Sigma$	22·16	...	...

According to this view, the fundamental level X $^1\Sigma_g^+$ of N_2 is formed by two N (^{4}S) atoms; this agrees with our picture of electron configuration because we can assume three electrons of one atom have all the spins ($+\frac{1}{2}$), while the three electrons have spin ($-\frac{1}{2}$). We thus get an inert gas-like structure for normal nitrogen molecule accounting for the inert properties of Nitrogen gas. The next level, *viz.*, $^3\Sigma$, which is the lowest of the triplet level, may be supposed to be due to the

combination of an N (^4S) atom and an N (^2D) atom. The formation of other levels, according to this view, is illustrated in Table 13. This enables us to fix up the combination for the other levels in the way as shown in Table 3.

13. Heat of Dissociation from Electron-Bombardment Data

An independent confirmation of the above value of heat of dissociation of nitrogen has been given by Mulliken[8] who bases his arguments on the data supplied by Tate and Lozier[72] on the determination of critical potentials of nitrogen by the electron-bombardment method.

In Lozier's[73] method electrons endowed with varying energy values were allowed to bombard the nitrogen molecules. As a result of the electron bombardment, molecules dissociated in a variety of ways. They found the minimum energy required to dissociate the nitrogen molecule into one neutral and one ionised atom of N. Like the mass spectrograph method of Hogness and Lunn[74] their experiments were also unable to determine uniquely the state of excitation of the products of dissociation and therefore the true heat of dissociation from the experimental data was merely conjectural.

If V_i be the minimum energy required to dissociate a molecule into N and N^+ and U_2-U_1 is the change in potential energy before and after the dissociation, the Kinetic energy of the products of dissociation is

$$\text{K. E.} = V_i - (U_2-U_1)$$

Since the mass of the dissociated atoms is the same, the kinetic energy V_F of one of the products would be given by

$$V_F = \tfrac{1}{2}\,[V_i - (U_2-U_1)]. \qquad (22)$$

If V_F is plotted against V_i the resulting graph would be a straight line cutting the V_i-axis at a distance U_2-U_1 from the origin Now U_2-U_1, the change in potential energy before and after the dissociation, gives $D_M + I_A$, where D_M is the heat of dissociation of the molecule and I_A is the ionisation potential of the atom, provided the N_2 molecule dissociates into N and N^+, so that

$$U_2-U_1 = D_M + I_A \qquad (23)$$

To obtain the value of $U_2 - U_1$ they employed the following method :—

A beam of electrons of varying energy values were accelerated axially into a cylindrical copper vessel and the positive-ion current was measured by an electrometer for different values of retarding potentials applied to the positive ions. This retarding potential was a measure of the K. E. of the products of dissociation. The positive-ion current was then plotted against varying electron energies for a given retarding potential. From this graph the minimum electron energy required to obtain the products of a given K. E. was found out. Next, the kinetic energy V_F was plotted against the minimum electron energy V_i and the intercept on the V_i -axis of the resulting straight line gave $U_2 - U_1$. It was found that the mean value of this intercept was $22{\cdot}9 \pm 0{\cdot}5$ volts, *i.e.*, $U_2 - U_1 = 22{\cdot}9 \pm 0{\cdot}5$ volts. By using the equation (23) we get

$$D_M = 8{\cdot}4 \pm 0{\cdot}5 \text{ volts.}$$

Otherwise we have,

$$N_2 + (22{\cdot}9 \pm 0{\cdot}5) \text{ volts} = N(^4S) + N^+(^3P) + e$$

$$= N(^4S) + N(^4S) + 14{\cdot}5 \text{ volts} \quad . \quad . \quad . \quad (24)$$

for according to Hopfield[75]

$$N(^4S) + 14{\cdot}5 = N^+(^3P) + e \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Hence $\quad N_2 = N(^4S) + N(^4S) - (8{\cdot}4 \pm 0{\cdot}5)$ volts,

i.e., $\quad D_{N_2} = (8{\cdot}4 \pm 0{\cdot}5)$ volts.

Arnot[76] pointed out that the above experiments were not reliable because space-charge effect would tend to set radial potential gradient which would vitiate the measurements.

Lozier[72] contended that the inaccuracy was not due to space-charge effect but due to contact difference of potential between the different metallic parts of the apparatus. He therefore repeated the experiments with an apparatus made entirely of Tantalum and made a slightly different interpretation of the results obtained.

For a particular value of the kinetic energy of the ions the minimum electron energy of the bombarding electrons for the first appearance of N_2^+ ions was found out. Let this be denoted by V_M. Similarly, the minimum energy of dissociation of N_2^+ ion into N and N^+ was also found out. Let this be denoted by V_I. Now part of this difference $(V_I - V_M)$ goes

to increase the potential energy of the molecular ions and the remainder into the kinetic energy of the products of dissociation. Therefore to dissociate the molecular ion N_2^+ the energy required would be $(V_I - V_M) - 2$ K.E. Lozier found that to dissociate N_2^+ into N and N^+ 8·62±0·02 volts were required, so that

$$V_I - V_M - 2K.E. = 8·62 \pm 0·02 \text{ volts.} \quad . \quad . \quad . \quad (26)$$

Assuming the N^+ ion in the excited state ^1D and N atom in the normal state ^4S Lozier got $D_{N_2} = 7·90$ volts.

R.S. Mulliken[18] assumed the products to be $N^+(^3P)$ and $N(^2D)$, which is in harmony with Herzberg's[19] assumption that the X′ level of N_2^+ is made up of $N^+(^3P)$ and $N(^2D)$ (*vide* infra)

$$N_2^+ + (8·6 \pm ·02)\text{volts} = N(^2D) + N^+(^3P) \quad . \quad . \quad . \quad (27)$$

$$N(^2D) = N(^4S) + 2·37$$

$$\text{or} \quad N_2^+ + (8·6 \pm ·02) = N(^4S) + N^+(^3P) + 2·37.$$

Further

$$N_2^+ = N_2 + 15·65 - e \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

and

$$N^+(^3P) = N(^4S) + 14·5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

$$\therefore \quad N_2 + 15·65 + (8·6 \pm ·02) = N(^4S) + N(^4S) + 2·37 + 14·5$$

$$\text{or} \quad N_2 = N(^4S) + N(^4S) - 7·42.$$

i.e., $D_{N_2} = 7·42$ volts.

The value of $I_M = 15·65$ volts employed above was obtained by Tate, Smith and Vaughan.[77] Now we know that the value of the ionisation potential of the molecule obtained from Hopfield-Rydberg series is 15·52 volts (*vide* § 5). Applying this in the above calculation Mulliken got $D_{N_2} = 7·28 \pm 0·02$ volts, which is in very good agreement with Herzberg's and Sponer's value from the predissociation phenomenon.

14. General Review of the Older Results of the Heat of Dissociation of N_2

In the following pages we shall attempt to review briefly some of the more important earlier methods for finding out the heat of dissociation of N_2. For the sake of completeness we give below in a tabular form the results of different observers using different methods: such a table was drawn some time back by A. K. Dutta[78] in this laboratory, but since then much important work has been done and the new material is included in Table 14.

Table 14.—Different methods of measuring the heat of dissociation of Nitrogen.

Author	Method	Reference	D_{N_2} in volts
Eucken[79]	Thermal	*Leibig. Ann.*, **44**, 111, 1924.	19·1 to 16·5
Langmuir[80]	„	*J. Am. Chem. Soc.*, **37**, 417, 1915	>10
Dutta[78]	Photodissociation of N_2O	*Proc. Roy. Soc.*, **138**, 84, 1932	8·7
Henry[81]	„ „	*Comptes. Rendus*, **200**, 656, 1935	6·85
Henry[81]	„ „	*Nature*, **134**, 498, 1934	6·9
Sponer[51]	Active Nitrogen	*Zeits. f. Phys.*, **34**, 622, 1925	11·4
Cario & Kaplan[82]	„ „	*Nature*, **121**, 906, 1921	9·6
Gaviola[83]	Sensitised fluorescence	*Nature*, **122**, 313, 1928	9·3 or 9·8
Birge & Sponer[10,16]	Extrapolation Method	*Zeits. f. Physik*, **41**, 611, 1927	11·75
„ „	„ „	*Phys. Rev.*, **28**, 259, 1926	11·4
Herzberg[84]	Discussion of N_2^+ bands	*Nature*, **122**, 505, 1928	9·1
Birge & Mulliken[85]	General Criticism	*Nature*, **122**, 842, 1928	9·5
Birge[86]	„ „	*Phy. Rev.*, **34**, 1062, 1929	9·0
Mulliken[18]	„ „	*Phys. Rev.*, **46**, 144, 1934	**7·40**
Turner & Sampson[87]	Excitation potential of N_2^+ bands	*Phys. Rev.*, **34**, 747, 1929	8·4
Grim[88]	Electron Bombardment	*Zeits. Electro. Chemie.*, **31**, 474, 1925	15·9
Tate and Lozier[73]	„ „	*Phys. Rev.*, **39**, 254, 1932	8·4
Lozier[72]	„ „	*Phys. Rev.*, **44**, 575, 1933	7·9
Lozier[89]	„ „	*Phy. Rev.*, **45**, 840, 1934	7·9 or 7·4
Herzberg & Sponer[66]	Predissociation	*Zeits. f. Phys. Chem. B.*, **26**, 1, 1934	**7·34**
Kaplan & Van der Ziel[67].	„	*Nature*, **133**, 416, 1934	**7·32**
Büttenbender and Herzberg[45]	„	*Ann. der Phys.*, **21**, 77, 1934	**7·34±0·05**
Watson & Koontz[71]	„	*Bl. Am. Phys. Soc.*, **9**, 12, 1934	7·9

It is interesting to note that each attempt to obtain an improved value of the heat of dissociation of nitrogen has led to a decrease in its former value. Thus, in the earliest attempts of Eucken[97] and Langmuir[80] who tried to deduce D_{N_2} from thermal dissociation, values between 10 to 19 volts were obtained. Soon after this Sponer[51] performed experiments on active nitrogen and assuming that the activity was due to atomic nitrogen found the heat of dissociation to be 11·4 volts. Birge and Sponer[16] then proceeded to determine the heat of dissociation by the well-known method of extrapolation of vibrational levels. In their first attempt, they obtained for the heat of dissociation of the level X′ of the ionised molecule (see diagram) a value of 9·1 volts and for the level A′ a value *lying between 3·16 to 7·7 volts*. As usual, assuming the ground level X′ of the ion to be composed of one normal neutral and one normal ionised atom, Birge and Sponer thought that the extrapolated value of 9·1 volts was the heat of dissociation of the molecular ion N_2^+ into a normal ($^4S_{\frac{3}{2}}$) N-atom and a normal ^3P (N^+-ion). Herzberg[19] showed (see later) that this was not a correct interpretation. Now, to obtain the heat of dissociation of the normal N_2-molecule, they used the relation

$$D_{N_2^+}+I_m=D_{N_2}+I_A \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

where

I_m = Ionisation potential of the Molecule.

I_A = " " " " Atom.

This can be proved as follows:—

$$N_2+D_{N_2}=N(^4S)+N(^4S). \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Adding to this I_A, we have

$$N_2+D_{N_2}+I_A=N(^4S)+N^+(^3P)+e. \quad . \quad . \quad . \quad . \quad (30)$$

Now,

$$N_2^++D_{N_2^+}=N(^4S)+N^+(^3P)$$

Also $\quad N_2^+=N_2+I_m$

or $\quad N_2+I_m+D_{N_2}=N(^4S)+N^+(^3P) \quad . \quad . \quad . \quad . \quad . \quad (31)$

From (30) and (31) we obtain

$$D_{N_2}+I_A=D_{N_2^+}+I_m.$$

Thus Sponer, using $D_{N_2^+}=9·1$ volts, $I_m=16·7$ volts, $I_A=14·2$ volts, obtained the value of $D_{N_2}=11·4$ volts. Here the value of I_m is taken from the experiments of Hogness and Lunn.[74]

Next, Herzberg[19] showed that Birge and Sponer's assumption that the X′-level of N_2^+ is made up of $N(^4S_{\frac{3}{2}})$ and $N^+(^3P)$ is not correct. He extended the negative nitrogen bands to about 12 levels and established beyond doubt that the *ground level X′* of the molecular ion is formed of one excited atom in the ^2D-state and one unexcited ion in the ^3P-state, while it was the excited state A′ of N_2 which was composed of $N(^4S)$ and $N^+(^3P)$ atoms. It was shown in the following way:

The value of $D_{X'}$ is found by the extrapolation method to be 9·1 volts and that of D_{A}' is found to be 3·7 volts, as shown in Fig. 4. The energy of the (0, 0) band is 3·25 volts. So when the level A′ breaks up into its constituent atoms, the total energy is 3·7+3·2=6·9 volts above the ground level of N_2^+. But when X′ breaks up, the total energy required is 9·1 volts. Hence the products of dissociation of X′ are richer. As this value is close to $^4S-^2D$ of N, Herzberg concludes that X′ is made up of $N(^2D)+N^+(^3P)$ while A′ is made up of $N(^4S)+N^+(^3P)$. We have therefore to substitute 6·9 volts for $D_{N_2^+}$ in equation (29). We thus obtain

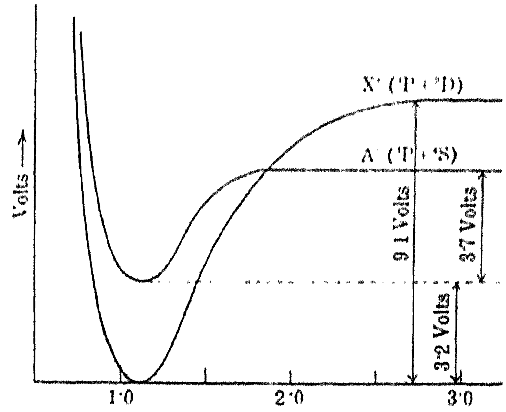

Fig. 4

$$D_{N_2}=16·7+6·9-14·5=9·1 \text{ volts.}$$

It is now clear that the value of I_m used in equation (29) and the later work of Birge and Mulliken is too large. We use the value obtained from Rydberg sequence, *viz.*, 15·5 volts. The value of I_A is now accurately known to be 14·48 volts. The only uncertainty lies in the calculation of $D_{A'}$. This is taken to be 3·7 volts. Thus we obtain, substituting these values in (29),

$$D_{N_2}+14·48=3·156+3·7+15·51$$

from which $D_{N_2}=7·88$ volts.

Taking into account the fact that in the above derivation of the heat of dissociation of N_2 the D for the upper state is obtained after all from a graphical method, the improved value of 7·88 volts seems to be in fair agreement with the present value. It rests entirely on the adjustment of the heat of dissociation of A′-state which in no case should exceed 3·11 volts in order to come up to the level of the recent value of 7·34 volts.

Soon after the announcement of the results of Birge and Mulliken the excitation potential of the Nitrogen molecule was found by Turner and Sampson[87] who employed a method of electron impact very much similar to Hertz's method for the determination of the ionisation potential of atoms.

Their object was to find out the minimum voltage required for the first appearance of the (0, 1) component at λ 4278·1 A°. U. of the negative bands of N_2^+. A mixture of 5 to 35% of nitrogen and neon gas at a total pressure of 0·25 mm. was bombarded by electrons emitted from an equipotential source. The bombarding electrons were given varying accelerating voltages. From photographs on different plates it was

observed that λ 4278·1 band appeared on an average of ·5 volts above the first appearance of the neon line λ 6402·2 which has an excitation potential of 18·5 volts. Thus it was concluded that the excitation potential of (0, 1) band of the Negative Group was 18·5 + ·5 = 19 volts. Now subtracting from this the excitation potential of 3·156 volts of the Negative Nitrogen bands we get 15·84 volts as the height of the level X' in volts above the ground level X' $^3\Sigma_g^+$ of the neutral molecule of N_2. Thus according to this method 15·84 volts is the ionisation potential of the nitrogen molecule.

Now Turner and Sampson used the extrapolated value of 3·7 volts as the heat of dissociation of the excited state A' and got D_{N_2} = 8·4 volts. But as remarked earlier this value is much above the mark. We can on the other hand use Mulliken's value of 6·31 volts for $D_{N_2^+}$ and the equation (29) to obtain D_{N_2} from the results of Turner. Then,

$$6{\cdot}31 + 15{\cdot}84 = D_{N_2} + 14{\cdot}48$$

$$D_{N_2} = 22{\cdot}15 - 14{\cdot}48$$

$$= 7{\cdot}67 \text{ volts.}$$

The cause of this high value of D_{N_2} even after making due improvement in the results of Turner is not far to see. It is due to the fact that the value of the ionisation potential I_m of the molecule is ·33 volts higher than the most recent value of 15·51 volts as pointed by Mulliken. This is not at all surprising for electron-bombardment results always give a value higher than the actual one. Thus, in a recent work, Sponer and Maier-Leibnitz[90] tried to find out the minimum excitation potential of the N_2 molecule (excitation from X to A) by the electron-bombardment method. This should be 6·14 volts according to Herzberg's theory, but the lowest value obtained by Sponer is 6·7 volts.

In conclusion, we wish to express our most cordial thanks to Professor M. N. Saha for invaluable guidance in the preparation of the present paper.

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THE CHEMICAL EXAMINATION OF THE FRUITS OF *LAGENARIA VULGARIS* SERINGE (BITTER VARIETY) PART I.—THE CONSTITUENTS OF THE OIL FROM THE SEEDS.

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Lagenaria Vulgaris, Seringe, commonly known in English as the gourd, *tumbi* in Hindi, and *Lau* in Bengali is a plant belonging to the natural order *Cucurbitaceæ*. The fruit of this is globular in size, some time enormously big and the shell of the dried fruit is commonly used as a vessel for holding all kinds of fluids in India and also for making guitars There are two varieties, a sweet one eaten as a wholesome vegetable by most Indians and the other a bitter one called *Karua-tumbi* in Hindi and *Tita-lau* in Bengali. The seeds of the fruit are greyish black, flat at the sides and elliptical, surrounded at times by a border which is inflated at the sides and notched at the apex, their kernels are white, oily and sweet. The seeds were originally one of the four cold cucurbitaceous seeds of the ancients. They still have a reputation of being very cold yielding an oil which is used as an application for headache. The pulp of the bitter variety is powerfully emetic and purgative. In Bombay it is used in native practice as a purgative.[1] Dr. B. Brown,[2] noticed the poisonous properties of the bitter variety the symptoms observed being similar to those after poisoning by elaterium or colocynth.

There appears to be practically no record of any work done regarding the chemical constituents of any part of this drug. Since the fruit still enjoys a reputation of being a purgative in Indian medicine, the present authors were tempted to put it, thoroughly, to a chemical examination. In the present paper an account of the chemical examination of the oil from the seeds is given The isolation, purification and constitution of the bitter principle from the pulp responsible for its purgative action will be described in a separate paper. The oil has been worked up in detail in the present investigation.

Experimental

34·25 kilograms of the fresh fruits (bitter variety) were obtained from the neighbourhood and the seeds removed. The dried seeds amounted to 2 kilograms. They were then finely crushed in an iron mortar and when burnt in a porcelain dish left about 12·2% of a greyish-white ash. The ash contained 41·0% of water soluble and 59·0% of water insoluble inorganic material. The ash had the following qualitative composition:

Potassium, sodium (traces), calcium (traces), aluminium, sulphates, phosphates, chlorides, carbonates and silica.

Extraction of the oil.—1·8 kilograms of the powdered seeds were then exhaustively extracted with benzene and 347 grams of a brown-yellow oil, having an odour reminding of the plant were obtained (19·1%). It was then purified with animal charcoal and Fuller's earth and obtained as a perfectly transparent light yellow oil. The oil on being kept deposited a very small amount (0·8g.) of a white sediment which proved to be an acid. The quantity obtained being very small nothing could be done to identify it.

Examination of the oil.—The oil contained no nitrogen or sulphur. It burned with a flame that was partly sooty and colourless. On examination it was found to be a semi-drying oil. Table I contains the usual physical and chemical constants of the oil.

Table I

Specific gravity	0·9051 at 29°C.
Refractive index	1·4620 at 30°C.
Solidifying point	−11°C.
Acid value	3·356
Saponification value	196·1
Acetyl value	18·2
Unsaponifiable matter	2 per cent
Hehner's value	93·2
Iodine value	105

135 grams of the oil were then saponified in the usual manner with alcoholic potash and the unsaponifiable matter extracted with ether in a big separating funnel. The fatty acids were then extracted in the usual manner, and Table II contains the physical and chemical constants of the generated fatty acid.

Table II

Consistency	Liquid
Specific gravity	0·9129 at 29°C.
Refractive index	1·3926 at 30°C.
Neutralisation value	199
Mean molecular weight	282
Iodine value	119

The mixture of the fatty acids (66 gram) were then separated into the saturated (solid) and unsaturated (liquid) acids by the Twitchell's lead salt alcohol method,[3] and Table III gives the percentage, iodine value and the mean molecular weight of the saturated and unsaturated acids.

Table III

Acids	Percentage in mixed acids	Per cent of the oil	Iodine value	Mean molecular weight
Saturated ...	52·47	47·8	4·15	263·9
Unsaturated ...	47·53	44·6	51·5	279·5

Examination of the unsaturated acids.—The constituents of the unsaturated acids were determined quantitatively by the method originally suggested by Eibner and Muggenthalor[4] and later on worked up extensively by Jamieson and Baughman.[5] According to this method the bromine addition products of the unsaturated acids were prepared as follows:—

To the known weight of the unsaturated acids dissolved in 150 cc. of dry ether, and cooled to $-10°$, bromine was added slowly, till it was in slight excess. During the process of bromination the temperature of the mixture was not allowed to rise more than $-5°$C. The mixture was then allowed to stand for two hours at $-10°$, in a frigidaire. Hexa-bromide, the bromo-drivative of linolenic acid is insoluble in ether. Since no precipitate insoluble in ether was formed, the absence of linolenic acid was confirmed. The ethereal solution was then treated with an aqueous solution of thio-sulphate in a separating funnel in order to free it from the excess of bromine. The ethereal solution was, next dehydrated by fused calcium chloride, filtered and the ether removal completely by evaporation. The residue was taken up

with about 200 cc. of dry petroleum ether, boiled in order to make a solution and kept in the frigidaire overnight. On standing linoleic-tetrabromide separated in fine glistening star-shaped needles, m.p. 112°C., which were filtered, washed and dried. The filterate and washings were collected together, concentrated to about 50 cc., cooled and again allowed to stand overnight. The second crop of tetra-bromide crystals obtained were added to the first and the whole thing weighed. Finally the petroleum ether filterate was evaporated to dryness and weighed. The bromine content of this residue was determined by boiling a small weighed sample with concentrated nitric acid and silver nitrate.

Table IV contains the results of the analysis of the bromine addition products.

Table IV

Weight of the unsaturated acids taken	4·6154 gm.
Linoleic-tetrabromide insoluble in petroleum ether .	3·6540 gm.
Residue (bi-bromide and tetra-bromide) . . .	6·0122 gm.
Bromine content of the residue	45·67 %
Di-bromo-oleic acid in the residue	2·3929 gm.
Tetra-bromo-linoleic acid in the residue	2·9631 gm.
Total tetra-bromo-linoleic acid	6·6171 gm.
Linoleic acid equivalent to the tetra-bromide. . .	3·0882 gm.
	or 66·91 %
Oleic acid equivalent to the di-bromide	1·5272 gm.
	or 33·09 %

The proportions of the linoleic and oleic acids in the unsaturated acids was also determined from the iodine value, of the liquid acids.

Table V contains the percentage of the linoleic and oleic acids in the unsaturated acids, and the percentage of their glycerides in the original oil, calculated by both the methods.

Table V

	Found % (Bromine addition products)	Found % (Iodine value)	Original oil %
Oleic acid ...	33·09	33·40	14·76
Linoleic acid ...	66·91	66·60	29·84

Examination of the saturated acids—The saturated acids separated by the lead salt alcohol method were freed from traces of liquid acid by pressing over porous plate. The acids thus obtained were perfectly solid, brownish white in appearance melting between 50–55°C.

The mixture of the saturated acids was converted into their methyl esters. The saturated acids were added in absolute methyl alcohol and a current of dry hydrogen chloride passed till it was saturated. The resultant mixture was heated over a water bath under reflux for about 15 hours. The esterified product was then neutralised with sodium-bi-carbonate and distilled water was added to it. The ester layer separated at the top and the aqueous liquid repeatedly extracted with ether. The ethereal solution was washed with water dried and the solvent removed by distillation.

The methyl esters obtained were subjected to fractional distillation under diminished pressure, the boiling points and the pressures being recorded. The iodine values and the saponification values of the different fractions were determined and the mean molecular weight calculated, using 56·1 as the molecular weight of potassium hydroxide. The M. W. of methyl palmitate is 270·3 and that of methyl stearate 298·4. The M. W. of the five fractions lie between these two values and indicate a mixture of the two. The M.W. of the last fraction is greater than 298 and hence contains the ester of an acid of greater M. W. than stearate, *i.e.*, arachidate. The percentages of the acids were determined in the different fractions by means of these mean M. W. and the iodine value.

Table VI contains the results of the fractionation and Table VII the results of analysis.

Table VI

Fraction	B. P.	Pressure m.m.	Weight in gm of the fraction.
1	160°—165°	0·5	29·25
2	165°–168°	0·5	19·20
3	168°–170° rose to 175°	0·5	8·680
4	175°–182° rose to 184°	0·5	3·090
5	184°–186°	0·5	4·420
6	186° rose to 190°–210°	0·5	9·970

Table VII

Fraction	Iodine Val	Sap. Val	Mean M.W.	Acids							
				Palmitic		Stearic		Arachidic		Unsaturated	
				Gms.	%	Gm.	%	Gm	%	Gm.	%
1	1·01	204·0	275·7	2·26	77·32	0·50	17·30	...		0·019	0·67
2	1·90	201·6	278·1	1·28	66·91	0·52	27·40		.	0·023	1·25
3	2·50	197·2	284·3	2·71	46·60	2·64	47·93	...	...	0·092	1·60
4	3·90	190·0	294·4	0·40	13·18	2·56	81·23	...	...	0·079	2·57
5	6·20	188·3	296·9	0·22	6·53	2·88	84·38		..	0·140	4·09
6	18·90	187·1	301·7	...		7·40	74·32	0·23	8·11	0·140	13·43
				5·87		9·50		0·23		0·493	

The percentage of various acids in the total saturated acids is given in Table VIII.

Table VIII

Acids.	% Found in the sat. acids	% in the original oil
Palmitic	36·48	17·62
Stearic	59·05	28·25
Arachidic	1·43	0·68
Unsaturated	3·04	1·45

Examination of the unsaponifiable matter.—The unsaponifiable matter (2 %) obtained from the soap solution by means of ether was washed in ethereal solution repeatedly with water. The dried ethereal solution was next distilled when white waxy flakes were obtained. It was crystallised from acetone. On recrystallisation from alcohol colourless crystalline needles were obtained melting at 131-132°C. It was identified as sitosterol.

SUMMARY

The oil from the seeds of *Lagenaria Vulgaris* Seringe has been examined in detail. The presence of the following substances has been established, and their percentages determined

Oleic acid	15·26%
Linoleic acid	30·74%
Palmitic acid	17·62%
Stearic acid	28·25%
Arachidic acid	0·68%
Unsaponifiable Matter Sitesterol	2%

ACKNOWLEDGEMENT

One of the authors (R. R. A.) is highly indebted to the 'Kanta Prasad Research Trust' of the Allahabad University for a scholarship which enabled him to undertake this problem.

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COLOUR AND CONSTITUTION OF DYESTUFFS DERIVED FROM FLUORENONE

By Mohit Kumar Mukherjee and Sikhibhushan Dutt,

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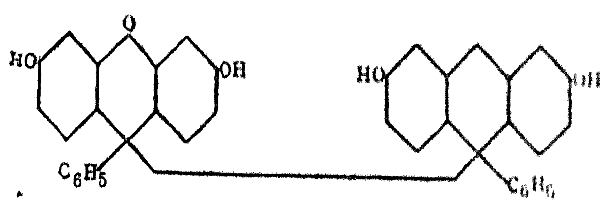
Received July 19, 1935

The phthalein type of dyestuffs have been known for a very long time, the first phthalein—fluorescein—having been prepared by Bayer in 1872. Since then almost all anhydrides of dibasic acids, saturated or unsaturated and belonging to the aliphatic, aromatic or heterocyclic series have been condensed with aromatic amino and hydroxy compounds with formation of dyestuffs. The pyronine type of dyestuffs obtained by condensations of aldehydes with aromatic amino and hydroxy compounds were first prepared by Otto Fischer in 1875, and although the number of such compound has been extended by later workers, yet they seem to have received far less attention at the hands of chemists than the phthaleins.

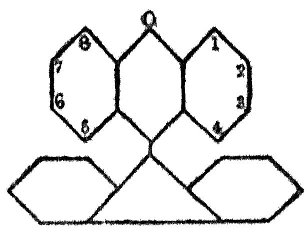
Very little attention has however been paid to the ketones as a source of dyestuffs. The first successful attempt in this connection seems to be that of Hans Von Liebig,[1] who prepared by heating together a mixture of benzil and resorcinol with or without the addition of fused zinc chloride, the compound:



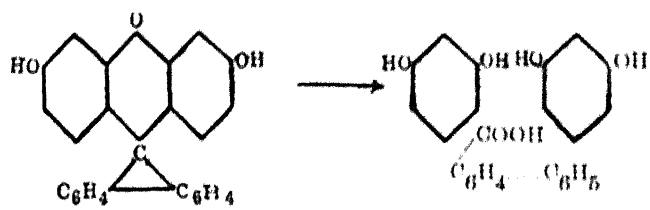
This has been described as similar to fluorescein in properties. Later on Scharwin and Kusnez[2] prepared from anthraquinone and resorcinol a condensation product very similar to the above. Very recently, Sen, Chattopadhaya and Sen Gupta[3] have prepared a number of pyronine dyestuffs from several aliphatic and aromatic ketones, such as acetone, diethyketone, acetophenone, benzophenone etc. The condensations were effected by heating with zinc chloride. The properties of most of the substances were closely analogous to the corresponding phthaleins.

The neglect which this class of compounds has received at the hands of colour chemists is apparently due to the fact their constitution is not amenable to a representation in the quinonoid form, which has invariably been thought to be the cause of colour of the pyronines and phthaleins.

The present investigation was undertaken to prepare dyestuffs from the interesting cyclic ketone, fluorenone, and to find out whether they correspond in properties to the analogous phthaleins or pyronines. The condensation products, which are easily obtained and which have the following skeleton structure,—



have been named—diphenylene-xanthenes for obvious reasons They have properties very similar to the pyronine dyestuffs, as will be apparent from the experimental parts of the paper. The constitution of the compounds is apparent from the fact that on fusion with caustic soda, all of them undergo fission with formation of the phenol from which they were formed and diphenyl-o-carboxylic acid. Thus 2:7-dihydroxy-diphenylene-xanthene (from resorcinol and fluorenone) on fusion with caustic soda yields resorcinol and diphenyl-o-carboxylic acid in the following manner:



The above constitution for the resorcinol compound is further corroborated by the fact that it forms a disodium salt and also a dibenzoyl derivative. All other hydroxy compounds also behave similarly.

A comparison of the dyestuffs derived from fluorenone with the corresponding phthaleins shows that in general the colour and intensity of fluorescence of the former is much less than the latter. But never-the-less the relation between the positions of the absorption maxima is about the same in both the series of dyestuffs. From this also it appears quite conclusive that apart from the difference in the intensity of colour and fluorescence caused by the use of different starting materials, there is no

fundamental difference in the constitution of the two types of colouring matters.

Another very interesting fact that has been found out in connection with the present investigation is the effect of different groups or radicals on the pyronine nucleus. Thus the condensation products of acetone, methylethylketone, diethylketone, benzaldehyde, acetophenone, benzophenone and fluorenone with resorcinol although have quite analogous constitution yet their absorption maxima is very different from one another as will be apparent from the following table:—

Dyestuff from	Absorption maxima	Dyestuff from	Absorption maxima
Acetone ...	4290	Acetophenone ...	5030
Methylethylketone	4680	Benzophenone ...	5185
Diethylketone ...	4740	Fluorenone ...	4185
Benzaldehyde ...	4940		

From the above figures, the gradual increase in the colour with the increase of the molecular weight of the radicals attached to the main xanthene nucleus will be apparent. The increase is not of course gradual as could have been expected by calculation. Actually in the case of the acetone compound the substitution of one methyl for ethyl, produces a jump in the absorption, but changing the other methyl to ethyl also, brings about a comparatively small effect Similar is in the case of substitution of a phenyl radical. But it is exceedingly interesting that two coupled benzene nuclei in the case of the fluorenone compound should produce such a remarkable lowering of the intensity of colour as compared with the benzophenone derivative.

The dyestuffs derived from fluorenone as also similar compounds derived from other ketones are undoubtedly non-quinonoid in character, since it is not possible to attribute to them any quinonoid configuration even with a considerable stretch of imagination. But never-the-less they have properties perfectly analogous to the phthaleins which have been definitely proved to have quinonoid constitution by a number of authors

The following aromatic amino and hydroxy compounds have been condensed with fluorenone and the following dyestuff obtained: resorcinol, catechol, orcinol, pyrogallol, phloroglucinol, *m*-dimethylamidophenol and *m*-diethylamidophenol. The hydroxy compounds have in most cases

been dibrominated and their disodium salt and dibenzoyl derivative been obtained. The condensations have invariably been effected by hydrogen chloride at 180—200°.

Experimental

Several condensing agents were tried for bringing about the reaction between fluorenone and aromatic hydroxy and amino compounds, *e.g.*, sulphuric acid, anhydrous zinc chloride, hydrogen chloride, acetic anhydride etc. In all cases zinc chloride and hydrogen chloride were found to be most effective. But when zinc chloride was used, a small residue of zinc always remained in the condensation product in spite of all attempts to eliminate the same. Consequently hydrogen chloride was used in all the cases. The general method of condensation consisted in taking one molecule of fluorenone and two molecules of the phenol or amino-phenol in a test tube immersed in an oil bath heated at 180—200°, and when the mixture had melted, in passing dry hydrogen chloride through the molten mass until complete condensation was effected. The usual period of heating varied from three to five hours. For the sake of abbreviation only a brief description of the properties of the condensation products are given.

2: 7-dihydroxy-diphenylene-xanthene.—Prepared from resorcinol and fluorenone. It crystallised from benzene in yellow prisms melting at 232°. It is fairly soluble in most of the organic solvents, but insoluble in water. The colour of the solution is bright yellow, and it shows a moss-green fluorescence. Solutions in caustic alkalies have only slightly deeper colour and fluorescence. (Found: C 82'17, H 4'30; $C_{25}H_{16}O_{4}$ requires C 82'4, H 4'39%)

The *dibromo derivative* was prepared from the resorcinol compound by adding an excess of bromine in alcoholic solution to the substance dissolved in alcohol. On allowing the mixture to stand at the ordinary temperature, the dibromo derivative crystallised out in reddish violet needles which were recrystallised from alcohol m.p. above 300°. The substance dissolves in most of the organic solvents and also in alkalies with a reddish pink colour and a pale green fluorescence. (Found Br 31'3; $C_{25}H_{14}O_{3}Br_{2}$ requires Br 30'41%).

The *disodium salt* was prepared by treating the dyestuff dissolved in absolute alcohol with the theoretical quantity of alcoholic caustic soda, and evaporating the solution. The crystalline substance was recrystallised from absolute alcohol in fine orange leaflets which did not melt on heating. (Found: Na 11'35; $C_{25}H_{14}O_{3}Na_{2}$ requires Na 11'27%).

The *dibenzoyl derivative* was prepared by the usual method and crystallised from pyridine in light yellow microscopic needles, melting at 212°. The substance is insoluble in alkalies. (Found: C 81·76, H 4·17; $C_{39}H_{24}O_5$ requires C 81·81, H 4·19%.)

1 : 8-dihydroxy-diphenylene-xanthene.—This was prepared from fluorenone and catechol. The substance crystallises from a large volume of water in long glistening golden-yellow needles containing a large amount of water of crystallisation. On drying in the steam oven or in the desiccator the water was lost and the substance was reduced to an orange-red powder melting at 169°. The substance is soluble in most of the organic solvents and also in water forming a bright yellow solution without any fluorescence. In caustic alkalies however an intense green colour is developed which is perfectly stable in the air. (Found: C 82·05, H 4·3; $C_{25}H_{16}O_3$ requires C 82·4, H 4·39%).

The *disodium salt* was prepared as before and crystallised from absolute alcohol in intense green crusts. (Found: Na 11·32, $C_{25}H_{14}O_3Na_2$ requires Na 11·27%).

The *dibenzoyl* derivative was prepared as usual and crystallised from pyridine. Light yellow powder, M.P. 141°. (Found: C 81·89, H 4·17; $C_{39}H_{24}O_5$ requires C 81·81, H 4·19%.)

The *dibromo* derivative was obtained as before and crystallised from alcohol in yellow prisms which did not melt even at 300°. It gives bright orange-red solutions in alkalies. (Found: Br 31·1; $C_{25}H_{14}O_3Br_2$ requires Br 30·4%)

2 : 7-dihydroxy-4 : 5-dimethyl-diphenylene-xanthene.—This was prepared from fluorenone and orcinol. It crystallised from alcohol in light brown microscopic needles melting above 300°. In properties it is very similar to the resorcinol compound. (Found: C 82·8, H 5·16; $C_{27}H_{20}O_3$ requires C 82·65, H 5·1%)

1 : 2 : 7 : 8-tetrahydroxy-diphenylene-xanthene was obtained from fluorenone and pyrogallol. It crystallises from large volume of water in shining yellow needles melting at 181°. The substance dissolves in alkalies with a dark reddish brown colour and from the solution a chocolate-brown precipitate is obtained on acidification. (Found: C 76·10, H 4·09; $C_{25}H_{16}O_5$ requires C 75·75, H 4·04%.)

The *disodium salt* was prepared as usual and was obtained from alcohol as a brown powder extremely soluble in water. (Found: Na 10·53; $C_{25}H_{14}O_5Na_2$ requires Na 10·45%.)

2 : 4 : 5 : 7-tetrahydroxy-diphenylene-xanthene was prepared from fluorenone and phloroglucinol. It could not be crystallised, but was

obtained from alcohol as a light brown powder melting above 300°. It dissolves in organic solvents to a bright yellow solution possessing a feeble green fluorescence. In caustic alkalies the colour is orange-red and the fluorescence is also more intense (Found: C 75·72, H 4·02; $C_{25}H_{16}O_5$ requires C 75·75, H 4·04%).

2 : 7-tetramethyldiamido-diphenylene-xanthene.—This was prepared from fluorenone and *m*-dimethylamidophenol. The substance crystallised from alcohol in violet-red prisms melting at 111°. The substance is soluble in all the organic solvents and also in dilute acids with a bright pinkish red solution with a dull yellow-brown fluorescence. (Found: N 6·6; $C_{29}H_{26}ON_2$ requires N 6·69%.)

2 : 7-tetraethyldiamido-diphenylene-xanthene.—This was prepared from *m*-diethylamidophenol and fluorenone. It crystallised from alcohol in dark violet crusts melting at 127° and had properties similar to the above compound. (Found: N 5·82; $C_{33}H_{34}ON_2$ requires N 5·90%.)

Absorption maxima of dyestuffs derived from fluorenone.

Dyestuff derived from fluorenone and	Absorption maxima
Resorcinol	4195
Ditto, dibromo derv.	4260
Catechol	4619
Ditto, dibromo derv.	4740
Pyrogallol	4535
Ditto, dibromo derv.	4696
Phloroglucinol	4219
m-Dimethylamidophenol	5074
m-Diethylamidophenol	5086

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THE CHEMICAL EXAMINATION OF PUNARNAVA OR *BOERHAAVIA DIFFUSA* LINN. PART II. THE ISOLATION OF AN ALKALOID PUNARNAVINE

By Radha Raman Agarwal and Sikhibhushan Dutt

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Received September 10, 1935

In a previous communication Agarwal and Dutt[1] in the course of their investigation on the chemical constituents of *Boerhaavia diffusa* Linn, (N.·O. Nyctaginæ) isolated from it a substance of the nature of an acid called by them Boerhaavic acid and reported that the drug contains a large amount of potassium nitrate which is responsible for the alleged diuretic properties. However, Ghosal[2] in the course of his chemical examination of this plant observed that it contained a sulphate of a body alkaloidal in nature. More recently Chopra, Ghosh, Ghosh and De[3] in investigating the pharmacology and therapeutics of this important medicinal plant reported that the drug contains an alkaloid called by them punarnavine and the diuretic action of the drug is due to this alkaloid in conjunction with potassium nitrate and other potassium salts. In the previous communication we (Agarwal and Dutt, *loc. cit.*) also showed qualitatively that the plant contains an alkaloid and gave a series of colour reactions with important alkaloidal reagents but failed to isolate it. In the present paper the alkaloid has been isolated in a pure form and a large number of its reactions recorded. The yield of punarnavine (·01) being very small nothing more could at present be done. Chopra and others (*loc. cit.*) did not isolate the free base or its hydrochloride in a sufficiently pure state to describe their properties, and used the aqueous solution of the hydrochloride for all their pharmacological work. We have been successful, by an improved method, to isolate the free base in a crystalline form from alcohol (see plate) and also its hydrochloride.

Experimental

Isolation of Punarnavine:—8 kg. of the dried and finely powdered drug was exhaustively extracted with boiling alcohol in a big extraction flask. The combined alcoholic extract on concentration to one-fifth of its volume and cooling deposited a dirty white crystalline stuff which was filtered, washed and dried. It was the boerhaavic acid contaminated

with chlorophyll and inorganic materials previously reported by us (Agarwal and Dutt *loc. cit.*). Finally the filtrate was completely evaporated to dryness on a water bath. The extractive was of a dark green colour smelling strongly of sugars and weighed 998 grams. This green sticky mass was repeatedly extracted with hot distilled water and the aqueous extract filtered. The neutral filtrate was concentrated to a small volume over a water bath and on cooling a large amount of greyish white material separated. This stuff was recrystallised from water and was found to be potassium nitrate. The potassium nitrate free concentrated extract was next made slightly alkaline with ammonia in order to liberate the free base and extracted repeatedly with chloroform in a big separating funnel till the chloroform extracts gave no tests for alkaloids. The chloroform extracts so obtained were carefully dehydrated by means of fused calcium chloride, filtered and evaporated to dryness whereby an yellow pasty mass of the base was obtained. The base was then repeatedly macerated with dry ether. Ether gradually removed the alkaloid and the ethereal extracts on complete removal of the solvent gave the base in a brownish yellow amorphous form. On dissolving it in the least quantity of ethyl alcohol and allowing it to evaporate slowly the alkaloid was obtained in white shining needles which under a powerful microscope revealed the presence of well-defined rectangular plates (see the plate).

The original alcoholic extract of the drug from which the alkaloid was dissolved in hot distilled water, was then repeatedly extracted with hot dilute (2%) hydro-chloric acid, in order to remove the last traces of the base. The combined acid extracts was then made slightly alkaline with ammonia and extracted repeatedly with chloroform and treated as before. A further quantity of the alkaloid was obtained which was also purified and crystallised from ethyl alcohol. The yield of the alkaloid thus obtained amounted to 0·8 grams, *i.e.*, 0·01% of the original weight of the dried drug. Chopra and others (*loc. cit.*) named this alkaloid as *punarnavine* after the plant which is very popularly known as *punarnava* in Sanskrit, and we also retain that name.

Properties of Punarnavine

Punarnavine is a white crystalline substance crystallising in rectangular plates from ethyl alcohol. It shrinks at 187° and melts with decomposition at 235°. It has got no smell but a bitter taste. It is freely soluble in alcohol, water, chloroform and less so in ether and acetone. It gives a delicate green colour with alcoholic ferric chloride and hence is a phenolic alkaloid. It gave no precipitate with lead acetate. With concentrated

sulphuric acid a beautiful greenish yellow colouration was obtained which gave a precipitate on dilution with water. Concentrated nitric acid gave a deep red colour. Concentrated sulphuric acid containing a little potassium nitrate gave a faint orange colour. Concentrated sulphuric acid containing potassium di-chromate (0·5%) gave a light yellowish green colour. With concentrated hydro-chloric acid no colouration was obtained. Mayer's reagent gave a crystalline white precipitate, iodine dissolved in potassium iodide gave a brownish black precipitate. Phospho-molybdic acid gave a blue colouration with a gradual blue precipitate whereas phospho-tungstic acid gave a greyish white precipitate. With Dragendroff's reagent a brown precipitate was obtained, and with Mandelin's reagent a granular brown precipitate immediately formed.

Punarnavine-hydro-chloride

The hydro-chloride was prepared in the usual manner (0·1g). Punarnavine was dissolved in cold ethyl alcohol and alcoholic hydro-chloric acid was added to it, while the mixture was cooled in ice. After some time the hydro-chloride separated as white crystalline tufts melting at 135°C. The crystals are shown in plate 1.

Pharmacology of Punarnavine

The pharmacological action of punarnavine was studied thoroughly by Chopra and others (*loc. cit.*) and we deem it proper to mention some of the interesting results obtained by them. The alkaloid had marked effect on the respiratory system, the amplitude and frequency of the lungs being increased. Intravenous injection of the alkaloid in cats produced distinct and persistent rise of blood pressure and marked diuresis. The alkaloid was found to be not very toxic.

ACKNOWLEDGEMENT

One of the authors (R. R. Agarwal) is highly indebted to the "Kanta Prasad Research Trust" of the Allahabad University for a research scholarship which enabled him to take part in this investigation. He is also very thankful to Lt.-Col. R. N. Chopra of the School of Tropical Medicine, Calcutta, for much valuable information and to Dr. D. R. Bhattacharya for the micro-photograph.

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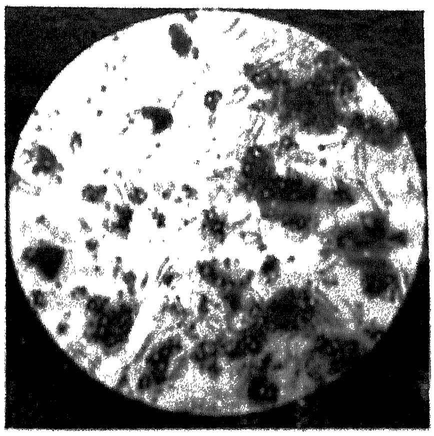

Punar-navine Crystallised from Alcohol

CONTRIBUTIONS TO THE DIGENETIC TREMATODES OF THE MICROCHIROPTERA OF NORTHERN INDIA

Part III.—New Distomes of the Genus *Mesodendrium* Faust (1919)

By B. P. Pande

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Communicated by Dr. H. R. Mehra

Received August 13, 1935

Introduction

The genus *Mesodendrium* was established by Faust (1919) for *Lecithodendrium granulosum* Looss, *L. hirsutum* Looss and *L. urna* Looss on the basis of the vitellaria being conspicuously posterior to the caeca near the acetabulum. Bhalerao (1926) added a fourth species, *M. attia*, from Burma. In another paper (1926, *a*) he referred to certain errors in the classification adopted by Faust and, considering the testes to be the most natural barrier to the extension of the vitellaria, he was of opinion that *Mesodendrium* should be distinguished from *Lecithodendrium* on the basis of its post-testicular vitellaria in the former; the vitellaria are pre-testicular in the latter genus. Following this scheme he included *L. ascidia* V. Beneden in *Mesodendrium* and retained *L. Urna* in the genus *Lecithodendrium*. Ozaki (1929) described two more species, *M macrostomum* and *M. spathulatum*, from Japan.

Mödlinger (1930), who redescribed *L. lagena* Brandes (1888)—a species considered previously by some authors as a synonym of *L. ascidia*, definitely confirmed Looss' observation (1899) that the vitellaria in *L. lagena* are post-testicular. It has been pointed out by me in the second part of this series of papers that *L. ascidia*, according to Mödlinger, has pre-testicular vitellaria and the synonymy of these two species, therefore, cannot be accepted. I am now definitely of opinion that *L. ascidia* belongs to *Lecithodendrium* while *L. lagena* is a species of the genus *Mesodendrium*. Stiles and Nolan (1931) obviously unaware of Mödlinger's paper proposed a new name for *lagena*, *i.e.*, *L. laguncula*. I referred to Dollfus' note on the synonymy of *Lecithodendrium* and *Mesodendrium* in a previous paper and pointed out that his genus *Prosthodendrium* cannot be

maintained. According to the classification adopted in part II and in this paper, only two genera, *i.e.*, *Lecithodendrium* and *Mesodendrium* are retained, the latter having *M. legena* as its genotype.

The present paper deals with two new species of the genus *Mesodendrium*, specimens of which were collected from the intestine of *Nycticejus kuhli* and *Vesperugo abramus*—the common insectivorous bats available in these parts. I am much indebted to Dr. H. R. Mehra for his constant help and guidance. Thanks are due to Dr. D. R. Bhattacharya for providing me laboratory facilities.

Mesodendrium modlingeri, n. sp.

Host—*Nycticejus kuhli.*

Position—Duodenum.

Locality—Allahabad.

These distomes, with plump and unflattened body, appear as white spots with a somewhat reddish-brown patch near the centre on the intestinal wall of the host to which they are firmly attached. The body, in the living condition, is active and distinctly cylindrical or flask-shaped, measuring about 1·04 in length and 0·6 in maximum breadth, which lies in the acetabular zone. The subterminal oral sucker, 0·08 × 0·1 in size, leads directly into a pharynx of 0·03 length and 0·04 breadth. The œsophagus, 0·11 in length, bifurcates into the caeca at one-fourth body length from the anterior end. The caeca lie more or less transverse to the body length. Unicellular glands are conspicuously developed in the forebody surrounding the pharynx, the œsophagus and the caeca. The acetabulum, situated near the middle of the body length, is about 0·1 in diameter. The genital pore lies median just in front of the acetabulum. The excretory bladder has the characteristic V-shaped appearance with the pore at the extreme posterior end of the body and the limbs reaching anteriorly as far as the posterior border of the testes.

The nearly rounded testes, with entire margins, lie symmetrically one on each side of the pseudocirrus-sac, the right testis measuring 0·15 × 0·17 and the left 0·15 × 0·14 in dimensions. The spherical pseudocirrus-sac, 0·17 in diameter, with a highly coiled vesicula seminalis, small pars prostatica, ejaculatory duct and a large number of well-developed prostate gland cells, lies between the acetabulum and the intestinal bifurcation.

The ovary, somewhat pear-shaped with irregular margins and 0·17 × 0·1 in size, lies just below the dorsal body wall slightly to the right

side in the acetabular zone. The shell gland complex is dorsally situated just behind the acetabulum and the ovary, internal to the latter. The receptaculum seminis is well developed and lies transversely in the shell gland area, measuring 0·05 × 0·07 in size. The uterus, in descending and ascending coils, fills up the entire post-acetabular space; the ascending limb extends to the posterior limits of the testes on its way to the genital pore. The metraterm is present. The vitellaria are composed of follicles arranged in a rosette-shaped manner and are in level with the posterior half of the ovary, those on the right side numbering 8-9 and of the left 7-8. A well-developed duct from each vitelline gland passes transversely behind the acetabulum to join at the shell gland area. The ripe, operculated eggs measure 0·02 in length and 0·01 in breadth.

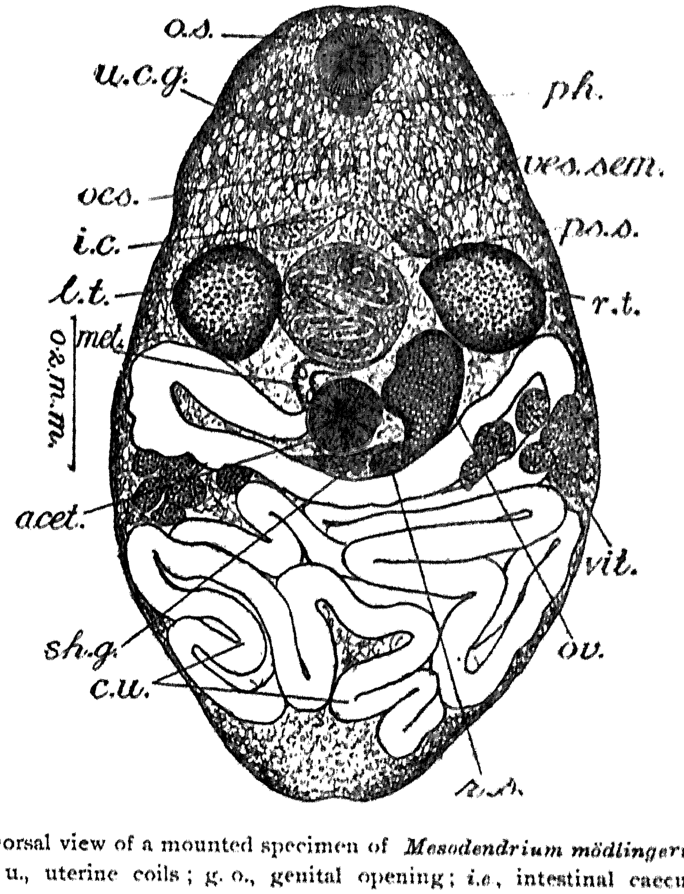

Fig. 1. Dorsal view of a mounted specimen of *Mesodendrium mödlingeri*, n. sp. acet., acetabulum; c. u., uterine coils; g. o., genital opening; *i.e.*, intestinal caecum; l. t., left testis; met., metraterm; oes., œsophagus; o.s., oral sucker; ov., ovary; p.g., prostate gland cells; ph., pharynx; ps. s., pseudocirrus-sac; r.s., receptaculum seminis; r.t., right testis; sh. g., shellgland-complex; ves. sem., vesicula seminalis; vit., vitellaria; y. d., yolk duct.

Remarks.—This species differs from the type species, *M. lagena*, in its shorter œsophagus, the position of the testes and ovary (the testes in *lagena* are placed on the sides of the acetabulum and the ovary close behind the latter). The presence of the receptaculum seminis in the type species is not mentioned, either in Looss' or in Mödlinger's descriptions. The new species can be distinguished from *M. hirsutum* by its smaller size, position of the acetabulum, testes, ovary, pseudocirrus-sac, and the presence of the receptaculum seminis. *M. granulosum* differs from it on account of its smaller size, its acetabulum being larger than the oral sucker, the position of the testes, smaller size of the receptaculum seminis and the larger number of follicles in the vitellaria. Bhalerao's species, *M. attia*, differs in its larger size, position of the acetabulum at about 1/3rd body length from the anterior end, shorter œsophagus, posterior limit of the intestinal caeca, position of the genital pore, testes and ovary and the arrangement of the vitellaria. The position of the testes and ovary and the absence of a receptaculum seminis distinguish the Japanese species, *M. macrostomum* and *M. spathulatum* from my species.

Mesodendrium elongatum, n. sp.

Host—*Vesperugo abramus.*

Position—Rectum.

Locality.—Allahabad

Body, 1·2 in length and 0·34—0·49 in maximum breadth which lies posterior to the acetabulum in the testicular and vitelline zones, is smooth, transparent, elongate and flattened. The subterminal oral sucker, 0·05-0·06 in length and 0·06--0·08 in breadth, leads into the spherical pharynx of 0·032—0·037 diameter. There is no prepharynx. The œsophagus, about 0 2 long, bifurcates into the intestinal caeca at about 1/4th body length from the anterior end. The caeca lie nearly transverse to the body length and end just in front of the genital pore. The acetabulum, smaller than the oral sucker, is situated at 1/3rd body length from the anterior extremity and measures 0·04—0·045 in diameter. The genital pore, nearly median in position, lies just in front of the acetabulum. The excretory bladder presents the typical V-shaped appearance with the pore at the extreme posterior tip of the body and the cornua extending forwards as far as the middle of the testes. The excretory pore leads into a small median stem which divides into the cornua, lying ventral to the vitellaria and the testes. A large number of unicellular glands is present in the body parenchyma anterior to the testes.

The testes, nearly rounded and smooth-margined, are situated behind the acetabulum somewhat diagonally to each other just in front of the

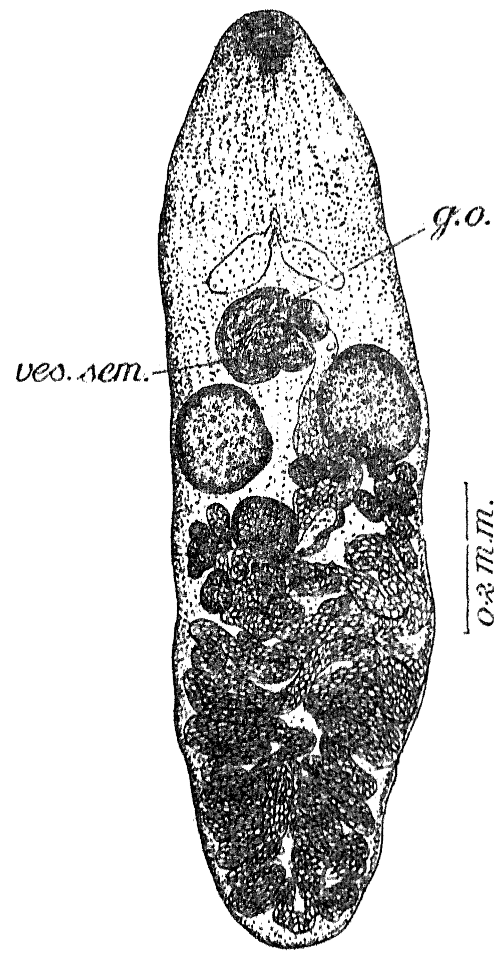

Fig. 2. Ventral view of a mounted specimen of *M. elongatum*, n. sp.

middle of the body length. The right testis measures 0·1—0·15 in length and 0·12 in breadth and the left 0·085—0·13 × 0·1—0·12 in size; the latter is slightly ahead in position to the right one.

The pseudocirrus-sac, with a much coiled and spacious vesicula seminalis, lies on the right side of the acetabulum between the right testis and the intestinal caecum. The vesicula seminalis, surrounded by the prostate gland mass, continues into the pars prostatica and the ejaculatory duct, the latter opening at the well-developed genital atrium.

The spherical and dorsally situated ovary lies behind the right testis and is about 0·09 in diameter. A receptaculum seminis is absent, the initial coils of the uterus serving as the receptaculum seminis uterinum. The Laurer's canal is present. The uterus, in descending and ascending coils, lies mainly behind the ovary lateral to and between the cornua of the bladder. The ascending limb of the uterus, lying near the ventral body wall in the inter-testicular space passes forwards to open at the genital atrium which lies below the pseudocirrus-sac. The vitelline follicles of the two sides are asymmetrical and lie just behind the testes; the group to the right has a smaller number of follicles and lies postero-lateral to the ovary. The ripe eggs measure 0·02 × 0·012 – 0·014 in size.

Remarks. The position of the gonads with the associated structures distinguishes this species from *M. lagena*, *M. granulosum* and *M. mödlingeri*. This species can be separated from *M. hirsutum* by the more posterior location of the testes and the ovary, and the asymmetrical vitellaria—the ovary in *M. hirsutum* lies a little behind the acetabulum in proximity with the posterior margin of the pseudocirrus-sac. The lateral position of the ovary, the greater length of the oesophagus, position and extent of the pseudocirrus-sac and the character of the vitellaria separate this species from *M. attia*. The Japanese species, *M. macrostomum* and *M. spathulatum*, differ from it in the position of the testes, pseudocirrus-sac, the ovary and the vitellaria.

In view of the previous work and my own observations, the diagnosis of this genus as given by Faust may be modified as follows:—

Diagnosis:—Small Lecithodendriinae; cuticle smooth, fore body with a large number of unicellular glands. Pharynx followed by a well-developed œsophagus; intestinal caeca terminating in front of or at the anterior margin of acetabulum. Genital pore, median or slightly lateral, close in front of acetabulum or between it and intestinal bifurcation. Testes, laterally situated, symmetrical or slightly asymmetrical, in acetabular plane or in front or behind it. Pseudocirrus-sac, with a large and coiled vesicula seminalis anterior or lateral to acetabulum. Ovary, dorsally situated, in level with acetabulum or behind it. Receptaculum seminis present or absent. Laurer's canal present Uterus, in descending and ascending coils, filling the entire post-testicular space, metraterm present. Vitellaria post-testicular. Excretory bladder V-shaped.

Habitat- intestine of insectivorous bats and chameleons

Locality—Europe, Egypt, India and Japan.

N.B.—All measurements in millimetres.

Addendum

In an abstract published in the Proceedings of the Eighteenth Indian Science Congress, Thapar reports a new trematode from *Nycticejus kuhli*. The detailed paper, so far as I know, has not been published. Thapar is certainly mistaken in believing that his form "conforms in general characters to the members of the family Dicrocoeliidae Odhner." The characters in which his specimens differ from the members of this family as given in the abstract are:—

1. The extra-cecal position of the testes.
2. Interceecal and post-testicular ovary.
3. Absence of an œsophagus or a prepharynx.
4. Presence of a descending and an ascending limb of the uterus

From the same host *Anchitrema sanguineum* Sonsino has been recorded by me (Pande, 1935). Very likely the distome reported by Thapar belongs to the genus *Anchitrema*, as the characters 1, 2 and 4 as given by him are present in this genus. I have pointed out in Part I of this series that Tubangui had also erroneously placed specimens of this genus under *Platynosomum* (Dicrocoeliinae). Regarding the 4th point of difference it may be pointed out that a short œsophagus is always present in this genus, but it is liable to be overlooked on account of contraction of the forebody during fixation; and further a prepharynx has not been described in the genus *Anchitrema*.

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Errata to Part I, Published in the Proc. Aca. Sci., U. P., Vol. 4, Part 4, pp. 371-380, 1935.

Page 371, line 13 from bottom, after "intestine of" add, "*Vesperugo abramus*, and."

Page 372, line 29 from bottom, for "*Nycticejus dormeri*" read "*Vesperugo abramus*."

THE GENITALIA AND THEIR RÔLE IN COPULATION IN *EPILACHNA INDICA* (COCCINELLIDAE: COLEOPTERA) WITH A DISCUSSION ON THE MORPHOLOGY OF THE GENITALIA IN THE FAMILY

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Introduction

While collecting specimens of Coccinellidæ during the months of August and September 1934, I came across several copulating specimens of *Epilachna indica*. This gave me an opportunity to observe the process of copulation closely and study the working of the various components of the genitalia in the process. The present paper embodies these observations.

The genitalia of some of the species of *Epilachna* have been described and sketched by previous workers but there are few references to any description of the rôle of the various sclerites in the process of copulation The only observation on the copulation of Coccinellids I could find is that by Sharp and Muir[1] who simply state "From observations of the copula of two or more species of Coccinellidæ, we find that the lateral lobes occupy a purely external position on the venter of the female." Furthermore, the musculature of the genitalia and the mode of working of the various muscles have also been insufficiently studied in the Coccinellidæ. The only description of the musculature of the Coccinellid genitalia known to me is that by Verhoeff[2] in *Coccinella septempunctata*, a species of the sub-family Coccinellinæ.

The male genitalia

The various sclerites of the Coccinellid genitalia have been differently interpreted and named by various observers; in fact, both their morphology and terminology have formed subjects of much dispute. In

this paper, however, I have used only such names as clearly express the functions of the sclerites concerned and are not objectionable from the viewpoint of their morphology.

The male genitalia of *Epilachna indica* (Fig. 1) consist of five distinct elements: 1. the sipho (*si*), 2. the basal piece (*b.p*), 3. the siphonal sheath (*s.sh*), 4. a pair of parameres (*pa.*), and 5. the median strut (*st*)*. The relations of these parts to one another can be seen by a reference to Figs. 1 and 3. In the normal position, all these elements are enclosed within a genital pouch (*g.p.*) which is a membranous sac arising from the end of the terminal body-segment and extending inwards so as to surround the genitalia up to the basal piece around which the inner end of the genital pouch is attached.

1. *The sipho* (*si.*, Fig. 1).—The sipho is an elongated tube, 3·3 mm in length, with a double curvature resembling more or less the letter S, the proximal and anterior curve being much more pronounced than the distal and posterior, which shows only a slight curvature.

The proximal end of the sipho widens out to form a boot-shaped siphonal capsule (*si. c*) about 0·24 mm. in diameter. The siphonal capsule bears two prominent projections (*c.pr*), the anterior being the larger of the two. The average thickness of the sipho is 0·07 mm. The common "ductus ejaculatorius" (*d.ej*) enters the sipho through a median foramen on the antero-ventral aspect of the siphonal capsule. In different preparations, it is possible to trace the ductus into the sipho for a considerable length, beyond which its walls become closely applied to those of the sipho and it is therefore not visible as a separate duct till it reaches the distal end of the sipho where it becomes distinct again. The distal end of the sipho is also expanded a little and forms a paw-like structure, 0·15 mm. in thickness; the dorsal surface of the paw projects a little beyond the ventral surface and both bear a number of recurved tooth-like structures some of which are larger than the others.

2. *The basal piece* (*b.p.*).—The basal piece is apparently made up of two lateral halves which, when seen from the dorsal side, appear like the two valves of a bivalve shell. Each half is more or less semi-cirular in shape and the two together form a box-like structure articulating

*These terms have been adapted from different authors: (1) Sipho (Verhoeff) represents the "median lobe" of Sharp and Muir and "penis" of some other authors. (2) Basal piece (Sharp and Muir) represents the "basal plat" of Verhoeff. (3) Siphonal sheath represents the "median lobe" of Sharp and Muir, the "basal lobe" of Wilson and the "penis" of Verhoeff. (4) Paramere represents the "parameron" of Verhoeff and the "lateral lobe" of Sharp and Muir. (5) Median strut represents the "trabes" of Verhoeff, the "strut" of Sharp and Muir and the "the tegminal strut" of some other authors.

postero-ventrally with the siphonal sheath described hereafter. Antero-ventrally the basal piece has a wide opening through which the sipho is retracted forwards into the body-cavity. Thus the ventral attachment between the two halves is only on the ventral corner of the basal piece.

3. *The siphonal sheath* (Figs. 1 and 2).—The siphonal sheath articulates postero-ventrally with the basal piece and surrounds the distal half of the sipho. It is about 1·5 mm. in length and about 0·2 mm. in thickness. Its distal end forms a hood-like structure, about 0·6 mm. in length; on its dorsal surface, it bears a number of long bristles while on its ventral aspect there is an elongated oval aperture (*o*), through which protrudes the distal end of the sipho. On the ventral surface of the proximal part of the siphonal sheath, there is an elongated slit (*sl.*) which is quite narrow proximally but widens out distally. Inside the siphonal sheath is seen another comparatively more delicate tube (*it*) surrounding the sipho. This inner tube is continuous distally with the siphonal sheath, while proximally it is continued beyond the basal piece as a very thin membranous tube surrounding the sipho (*it'*) right up to the siphonal capsule where it is attached.

4. ***The strut*** (*st*).—The median strut is an elongated S-shaped chitinous rod, one end of which articulates with the ventral corner of the basal piece and the other almost fits against the siphonal capsule.

5. *The parameres* (*pa*).—The parameres articulate with the postero-dorsal surface of the basal piece, one on each side. It should be noted here that the joint between the basal piece and the parameres shows differential chitinisation. On the postero-dorsal side, the chitin is thin and delicate while it is thick and strong on the opposite side. The result of this differential chitinisation is that in the natural condition the parameres remain inclined towards the siphonal sheath unless they are pulled away by muscular contraction. The significance of this mechanism will be described later in the section dealing with copulation. Each paramere is about 1·4 mm. in length and tapers towards its distal end, the thickness near the base being nearly 0·14 mm. while that near the end being only 0·06 mm. The distal end bears long bristles, while a few bristles are also present about the middle of the length.

The rod (*r.*, Fig. 4).—In *Epilachna indica* the rod originates at a point close to the origin of the genital pouch, on its left ventral aspect, and extends right up to the basal piece. It is a hollow structure, about 1·5 mm. in length, lying completely outside but close to the wall of the genital pouch. The inner end of the rod serves for the attachment of three sets of muscles (*r.m.* 1, 2, 3), which work the different sclerites of the genitalia.

Thus functionally at least, it may appropriately be called the *genital apodeme* serving for the attachment of genital muscles in exactly the same way as the head apodemes do for the muscles of the mouth-parts.

Musculature of the male genitalia and their mode of working

The muscles which effect the working of the different parts of the male genitalia may be described under the following names:—

1. The sipho-basal muscle (*s.b.*),
2. The sipho-strutal muscle (*s.st*),
3. The baso-parameral muscle (*b.p.m.*),
4. The rod muscles (*r.m.* 1,2,3),
5. The strutal muscle (*st m.*).

1. *The sipho-basal muscle* (*s.b.*). The muscle-bands of this set originate from anterior border of the siphonal capsule and run backwards on either side of the siphonal capsule to be inserted on the inner surface of the basal piece. Some of the muscle-bands run straight and are situated symmetrically both on the right and left sides of the siphonal capsule, while others run obliquely between these two straight muscle-bands. The combination of these straight and oblique muscle-bands is admirably adapted for the purpose of forcing the distal part of the sipho out of the siphonal sheath, and this is effected by a simultaneous contraction of these two kinds of muscles in this set.

2. *The sipho-strutal muscle* (*s.st.*). The bands of this muscle originate from the deep concavity in the siphonal capsule and are inserted fan-wise on the ventral edge of the median strut. The contraction of these muscle-bands first brings the siphonal capsule in contact with the median strut which now acts as a pivot, and then a further contraction of these muscle-bands serves to retract the sipho within the siphonal sheath. The attachment of this muscle on the median strut is so arranged as also to check the sipho from being forced out too much by the contraction of the sipho-basal muscle.

3. *The baso-parameral muscle* (*b.p.m.*). These muscle-bands originate from the inner surface of the basal piece and are inserted into the base of each paramere beyond the zone of weak chitinisation described above. The contraction of these muscles pulls the parameres backwards. The exact significance of this action will be described in the section dealing with copulation.

4. *The rod muscles* (*r.m.*).—There are three sets of rod muscles, all of which originate round the inner end of the rod. One of these sets is inserted on the strut (*r.m 2*). the other on the inner surface of the basal piece (*r.m.3*). and the third on the genital pouch surrounding the genitalia (*r.m.1*). The contraction of the first two sets serves to retract the whole of the genitalia inside the body, after they have been protruding out of the body during copulation. The function of the third set, however, is not clear; probably it helps in the retraction of the membrane on which it is inserted at the time of the protrusion of the genitalia during copulation.

5. *The strutal muscle* (*st.m*).—The bands of this muscle originate from the sides of the strut and are inserted symmetrically on both the right and the left sides of the genital pouch. The contraction of these musclebands together with that of the abdomen as a whole serves to protrude the genitalia out of the body.

The female genitalia

The female genitalia are illustrated in Fig. 5 (Pl. IV) and consist of a number of sclerites surrounding the genital opening.

There is no differentiated ovipositor. The female genital opening is bounded by an unpaired dorsal plate (*d. p.*) above, a pair of lateral plates (*l.p.*) on the sides and a pair of ventral plates (*v.p.*) below. The dorsal plate is almost semi-circular in shape, about 0·23 mm. in radius; the ventral plates are almost quadrilateral in shape and about 0·4 mm. by 0·5 mm. in dimensions; while the lateral plates are very irregular in shape and are larger in size than either the dorsal or the ventral ones. The genital opening is also strengthened by a chitinisation of its rim. The pair of ventral plates acts as a valve closing the genital opening in the normal position.

The female genital opening leads, without any intervening tube, into two different organs—one being the prominent bursa copulatrix (*b.c.*) and the other vagina (*v.g.*) which looks "funnel-shaped."* The bursa copulatrix receives, close to its anterior extremity, the short spermathecal duct which shows a brownish chitinisation at its two ends. There are also a few glandular structures near the opening of the spermathecal duct into the bursa but their nature and function are not clear.

*The term "funnel-shaped" has been taken from Dobzhansky's (5, 1931) account of North American beetles of the genus *Coccinella*.

The bursa copulatrix, although lying dorsal to the vagina, lies on the same level as the genital opening while the vagina is depressed and lies at a lower level.

Copulation

Copulating pairs were very common during August and the first half of September but only stray cases of copulating Epilachnids were observed during the latter half of September. Before the middle of September, even the same pair was observed to copulate twice or thrice during a period of 5 to 6 hours. In the laboratory they have not been observed to copulate before 9 A.M.

The male after seeking out the female touches the latter with its antennae for a second and then mounts on the body of the female from any direction. It now compresses its own abdomen in this position; this compression of the abdomen along with the contraction of the strutal muscles squeezes out the greater part of the genitalia. Now with the help of the protruded genitalia, the male tries for a time to find out the female genital opening, touching the body of the female at different places till the female genital opening is reached.

After orientating itself properly (Fig. 7), the male deflexes the parameres and places them beneath the last two sternites of the female (Fig. 8). This flexion downwards is accomplished (as indicated by a study of the musculature) by a contraction of the baso-parameral muscles. As the parameres reach the under-side of the abdominal sternites of the female, the baso-parameral muscles relax and the parameres get pressed against the sternites of the female (Fig. 8) on account of the differential chitinisation of the bases of the parameres which tends to keep the parameres pulled towards the siphonal sheath. While thus pressed against the sternites of the female, the ends of the parameres get a leverage against the articulation between the second and third abdominal sternites from behind At the same time, the siphonal sheath is applied against the ventral pair of plates of the female genitalia (*v.p.*, Fig. 6). While the genitalia are in this position, the parameres together with the siphonal sheath look like the three legs of a tripod, the two legs (*i.e.*, the parameres) being pressed against the female abdominal sternites and the third stouter leg (*i.e.*, the siphonal sheath) being similarly pressed against the ventral plates of the female genitalia; the three legs forming an excellent steadying apparatus. As this steady posture is attained, the sipho by a contraction of the sipho-basal muscle, is inserted into the female genital

opening through a small space left between the distal edges of the ventral plates of the female genitalia. Since the bursa copulatrix is in direct line with the genital opening, the sipho enters the bursa directly.

While the sipho is thus lodged in the bursa of the female, a wave of contraction is seen passing at quick intervals from the anterior to the posterior part of the male abdomen. This contraction most probably compresses the body fluid, and this compression together with the contraction of the strutal muscles keeps the genitalia as a whole forced out till the copulatory act is completed. The copulation lasts for five to ten minutes.

The actual extent to which the sipho penetrates the bursa has not been determined by me, nor have I been able to make sure whether there is any kind of evagination from inside the sipho or not. On killing the specimens, the muscles contract and the sipho is partly withdrawn; and as the pressure on the body fluid relaxes, the genitalia as a whole retract and are withdrawn into the body. But from the comparative size of the bursa and the sipho (Fig. 6) it can be confidently inferred that the sipho can at the most reach up to the inner end of the bursa and that it cannot enter the spermathecal duct. Further, the narrow bore of the spermathecal duct together with its somewhat chitinised nature would also support the view that the sipho cannot enter it. Thus the sperms are most probably not placed directly into the spermatheca at least in this species. Sharp and Muir could not be certain whether the sperms are deposited directly into the spermatheca or placed in some part of the female tube.

Oviposition

The eggs of *E. indica* are beautifully arranged in small clusters on the leaf of the food-plant (*Cucumis melo* var. *utilissimus*), each egg being fixed perpendicularly to the surface of the leaf (Fig. 9). The eggs are elongated oval in shape, about 1·5 mm. in length and 0·54 mm. in thickness. In egg-laying the female contracts its abdomen and one can observe waves of contraction passing from the anterior part of its abdomen to the posterior. It appears as if the insect is trying to squeeze something out of its body. As a result of these contractions, an egg is seen emerging from the female genital opening and by and by a large part of it comes out. At this time the elongated egg is horizontal in position but as the female raises the posterior part of its abdomen, the egg by its own weight becomes vertical in position, and while its one end is still enclosed in the

genital opening, the other end gets attached to the leaf. The final wave of contraction squeezes out the egg completely. After laying one egg, the female moves a little forwards and repeats the process. The result of these repetitions is a fine cluster of eggs arranged perpendicularly on the leaf. The eggs have also been found in a scattered condition but this is most probably due to the fact that the female has been disturbed during the act of egg-laying.

Discussion on the morphology of the genitalia.

Of the various sclerites of the genitalia, the homology of the sipho is most disputed. The three interpretations of its homology so far given are:—

1. Verhoeff suspected the sipho to be homologous with the flagellum of *Camptocarpus* and many other Coleoptera but did not feel convinced about it and therefore called it a new structure of unknown homology; he went further, as on this interpretation of his he divided the Coleoptera into two groups:—
   - (*a*) Siphonophora (Coleoptera with a sipho, including the single family Coccinellidæ).
   - (*b*) Asiphona (Coleoptera without a sipho, including the remaining families of Coleoptera).
2. Sharp and Muir homologised the sipho with the median lobe of the genitalia of other Coleoptera and regarded the siphonal sheath as a secondary development round the median lobe.
3. The third interpretation is by Dr. Klemm[3] who regards the sipho as having been derived by a lengthening of the thickened inner wall of the ductus ejaculatorius.

Verhoeff's interpretation that the sipho is the homologue of the flagellum of other Coleoptera is refuted by the following facts:—

(*a*) Within the sipho, the ductus ejaculatorius is distinctly traceable but in the flagellum the ductus ejaculatorius is always absent; the flagellum, in fact, is only a secondary hollow growth from the mouth of the ductus ejaculatorius.

(*b*) The flagellum is co-existent with the sipho in at least two species of Coccinellidæ,* *i.e. Chilomenes sexmaculata* (Fig. 10) and *Halyzia 18-guttata* (Fig. 11). In these species, the flagellum can be clearly distinguished from the sipho by the absence of the ductus ejaculatorius in the flagellum.

*The flagellum has been described in *H. 18-guttata* by Verhoeff but in *C. sexmaculata* I have observed the flagellum myself.

If we interpret the sipho as the homologue of the median lobe, as Sharp and Muir have done, we shall have the following difficulties :—

(*a*) We shall have to imagine that the median lobe, which in the rest of the Coleoptera remains almost firmly attached to the basal piece (Figs.13—18) very near and in between the parameres, has here suddenly been thrust far into the body cavity, leaving the basal piece and the parameres behind where they were. For this great displacement, there seems little ground. Not only there is no intermediate stage existent between the condition found in the Coccinellidæ and that in the rest of the Coleoptera, but we do not find even a tendency for this displacement in the rest of the Coleoptera. Such a sudden change, therefore, seems extremely unlikely.

(*b*) The fact that the flagellum starts directly from the end of the sipho both in *Chilomenes sexmaculata* (Fig. 10) and *H. 18-guttata* (Fig. 11) shows that the sipho cannot be homologised with the median lobe which is not directly continued into the flagellum in any of the species of Coleoptera; in fact, the flagellum always arises from the innermost end of the internal sac where the ductus ejaculatorius ends.

(*c*) Verhoeff's interpretation of the siphonal sheath as the penis (median lobe) cannot be ignored. The continuation of the membranous tube (*it′*, Fig. 1) with the inner tube (*it*, Fig. 1) inside the siphonal sheath suggests a strong resemblance between the median lobe and the internal sac of the Cucujidæ on the one hand and the siphonal sheath and the inner tube of the Coccinellidæ on the other.

Lastly, with regard to Dr. Klemm's interpretation, it will be enough to point out that the sipho cannot be a modification of the ductus ejaculatorius, since we find that the ductus is distinctly present and is easily traceable within the sipho.

In view of the anatomical facts mentioned above, it would seem that the views of the previous workers are not tenable. A comparison of the Coccinellid genitalia, firstly, with those of the several species of Cucujidæ, e.g., *Cucujus mniszechii* (Fig. 15), *Brontopriscus sinuatus* (Fig. 16), *Rhizophagus depresus* (Fig. 17), secondly, with that of *Camptocarpus prolongata* (Fig. 18, fam. Erotylidæ), and thirdly, with that of *Lucanus cervus* (Fig.13, fam. Lucanidae) suggests the following interpretations :

1. That the membranous tube (*it*,[1] Fig. 1) surrounding the sipho which Sharp and Muir have regarded as the connecting membrane between the tegmen (basal piece and parameres together) and the median lobe represents the wall of the internal sac.

2. That the flagellum of *Chilomenes sexmaculata* and that of *H. 18-guttata* are homologous with the flagellum found in other Coleoptera, *e.g.*, Cucujidæ, Erotylidæ, Lucanidæ, etc.

3. That starting with the type of genitalia found in the Cucujidæ the sipho of the Coccinellidæ has arisen by a partial evagination of the internal sac and a chitinisation of this evaginated portion. That this evagination has occurred elsewhere also is shown by the fact that in *Lucanus cervus* there has been a complete evagination of the internal sac. We thus have a case of partial evagination in the Coccinellidæ and that of complete evagination in *Lucanus cervus*.

There is no doubt that a part or whole of the internal sac is evaginated during copulation and that it is a very difficult operation to retract an elongated internal sac completely every time after copulation. One can imagine that the ancestors of Coccinellidæ were somehow not able to retract the whole of the internal sac every time after copulation and the result was that the part which remained evaginated, became gradually chitinised and formed the sipho. When the chitinised sipho was formed and used for insertion into the female genitalia, the flagellum was dispensed with in most of the Coccinellid species.

It may be noted that this interpretation of the origin of the sipho does not interfere with Sharp and Muir's general conclusions about the phylogeny of the Coccinellidæ based on their comprehensive studies, but falls in line with their view deriving the Coccinellidæ from forms such as the Cucujidæ.

As regards the homology of the siphonal sheath it is difficult to state a definite view. If the continuation of the membranous tube (internal sac according to the above interpretation) with the tube (inner) within the siphonal sheath is not secondary, we will have to admit that the inner tube within the siphonal sheath is also a part of the internal sac and that the internal sac originates from the end of the siphonal sheath which then will be homologous with the median lobe (penis) as Verhoeff has interpreted; but if the siphonal sheath is regarded as a secondary growth, the median lobe will have to be regarded as having been lost, its place being taken by the siphonal sheath. I feel inclined towards this latter possibility. The loss of the median lobe should not be surprising, if we bear in mind the fact that the median lobe has already been, comparatively speaking, very much reduced in the Cucujidæ.

On these considerations, I agree with Verhoeff that the sipho is not homologous with the median lobe but am not convinced at the same time that the sipho is a new structure. I regard the sipho as a chitinised part

F. 18

of the internal sac and believe that the mere fact of chitinisation of this part of the internal sac should not affect its homology. I find, therefore, no justification for Verhoeff's division of Coleoptera into two groups only on the basis of the presence or absence of the sipho. Verhoeff's separation of the Coccinellidæ from the rest of the Coleoptera implies that the Coccinellidæ diverged from the main stem prior to the evolution of the rest of the families of Coleoptera whereas the above-mentioned considerations show that the Coccinellidæ may well be regarded as having been evolved from forms like the Cucujidæ.

Material and Technique

The insects dissected during the present investigation were either brought fresh from the cucumber (*Cucumis melo* var. *utilissimus*) fields, wherein quite a large number of these insects were found during August, September and the first half of October, or were reared in the laboratory on cucumber leaves.

In the beginning, the insects were killed in KCN tubes but this method was found unsatisfactory, as the copulating pairs in the majority of cases separated on being put in KCN tubes. So, later on, the copulating pairs were killed by electrocution which was found to be a better method.

In order to study the rôle of the different muscle-bands in the protrusion and retraction of the genital sclerites, the following procedure was adopted :—In ascertaining, for example, the muscles concerned in the protrusion of the sipho, first a few incisions were made in the abdomen of a freshly killed insect; then the sipho was pulled out to the desired degree with the help of a pair of fine forceps; and while keeping the sipho in this condition the whole insect was fixed for 10 to 15 minutes in corrosive sublimate solution. Thus the effect of the artificial protrusion of the sipho on the different muscles was permanently fixed and could be studied later. Then by comparing the shape and size of the muscles thus affected by the pulling of the sipho with those of the muscles in the normal condition of rest, it was easy to ascertain the rôle of the muscles concerned in working the sipho. By studying the effect of artificial protrusion and retraction of the different sclerites on the muscles in this way, the functions of the latter became sufficiently clear.

The working of the muscles was also studied though with less certainty in ordinary dissections under a binocular microscope.

The structure of the chitinous parts was studied from specimens cleared in KOH solution (7·5%).

The drawings were made with the help of camera lucida from permanent balsam preparations.

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Explanation of Plates

Fig. 1. The male genitalia of *E. indica*. The rod is not shown. Side view. (×37½).

Fig. 2. The siphonal sheath of *E. indica*. Ventral view. (×37½).

Fig. 3. A diagrammatic representation of the position of the male genitalia of *E. indica* inside the abdomen. The genitalia have been shown in the vertical position but actually they lie flat, their left side being ventral and pressed against the wall of the genital pouch, when they are at rest. They assume the position shown in the diagram only just before being protruded out for copulation.

Fig. 4. The male genitalia of *E. indica* showing the musculature. The terminal body-segment has been retained; the genitalia have been turned on to the right to show the attachment of the rod. (×37½).

Fig. 5. The female genitalia of *E. indica*. Ventral view. (×56¼).

Fig. 6. The male and the female genitalia of *E. indica* in the copulating position. (37½).

Fig. 7. The copulating pair of *E. indica*. Lateral view. (× cir. 6½).

Fig. 8. The copulating pair of *E. indica*. Ventral view, showing the position occupied by the parameres during copulation. (× cir. 6½).

Fig. 9. The cluster of eggs of *E. indica* on the leaf of *Cucumis melo* var. *utilissimus*. (× cir. 6½).

Fig. 10. The male genitalia of *Chilomenes sexmaculata.* Side view. ($\times 37\frac{1}{2}$).

Fig. 11. The sipho of *Halyzia 18-guttata.* (After Verhoeft.)

Fig. 12. Hypothetical figure showing the similarity between the Coccinellid genitalia and those of *Lucanus cervus.*

Fig. 13. The male genitalia of *Lucanus cervus.* (After Sharp and Muir.)

Fig. 14. The male genitalia of *Mysia oblongoguttata.* (After Sharp and Muir.)

Fig. 15. The male genitalia of *Cucujus mniszechii.* (After Sharp and Muir.)

Fig. 16. The male genitalia of *Brontopriscus sinuatus.* (After Sharp and Muir.)

Fig. 17. The male genitalia of *Rhizophagus depressus.* (After Sharp and Muir.)

Fig. 18. The male genitalia of *Camptocarpus prolongata.* (After Sharp and Muir.)

Note.—The correct magnifications of figures as printed are given above; the magnifications given in the plates represent those of the original diagrams before reduction.

List of Abbreviations

a.	anus.
b.c.	bursa copulatrix.
b.p.	basal piece.
b.p.m	baso-parameral muscle.
cm.	connecting membrane.
c.pr.	projections on siphonal capsule.
d.ch.	differential chitinisation.
d.ej.	ductus ejaculatorius.
d.p.	dorsal plate.
d.sp.	duct of the spermatheca.
fg.	flagellum.
g.o.	opening of the genital pouch.
g.p.	genital pouch.
i.s.	internal sac.
it.	inner tube within the siphonal sheath.
it'.	membranous tube surrounding the sipho.
l.p.	lateral plate.

l.l. lateral lobe (paramere).
m.l. median lobe.
o. oval aperture in the siphonal sheath.
pa. parameres.
r. rod.
re. rectum.
r.m. rod muscles.
S.3-8. abdominal sternites.
s.b. sipho-basal muscle.
si. sipho.
si.c. siphonal capsule.
sl. slit in the siphonal sheath.
sp. th. spermatheca.
s.sh. siphonal sheath.
st. median strut.
s.st. sipho-strutal muscle.
su.p. suranal plate.
T.3-10 abdominal tergites.
vg. vagina.
st.m. strutal muscle.
v.p. ventral plate.

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S. PRADHAN

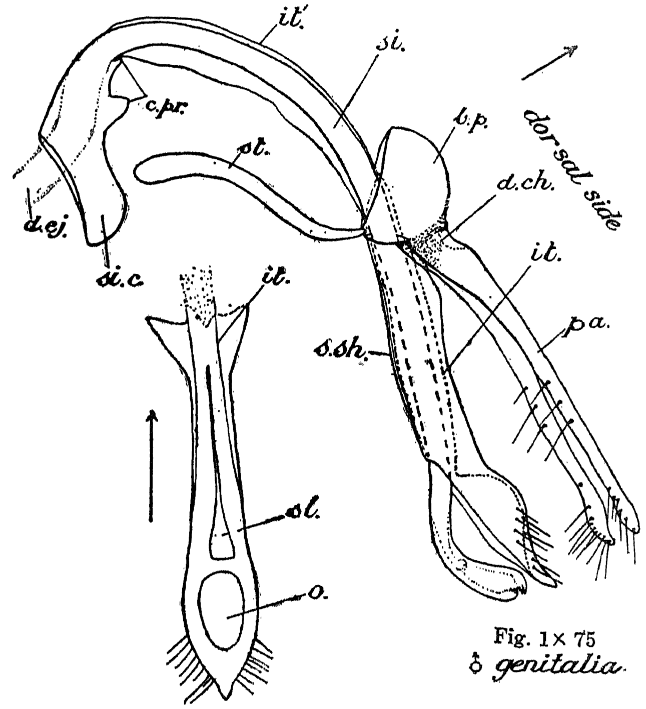


Fig. 1 × 75
♂ genitalia.

Fig. 2 × 75

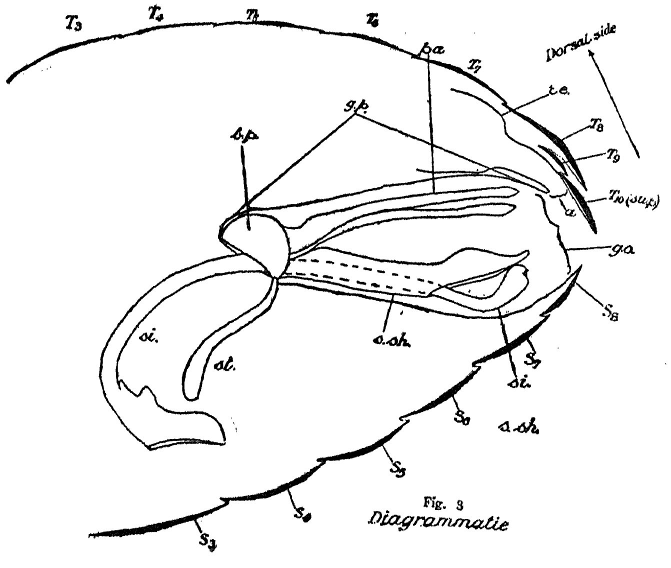
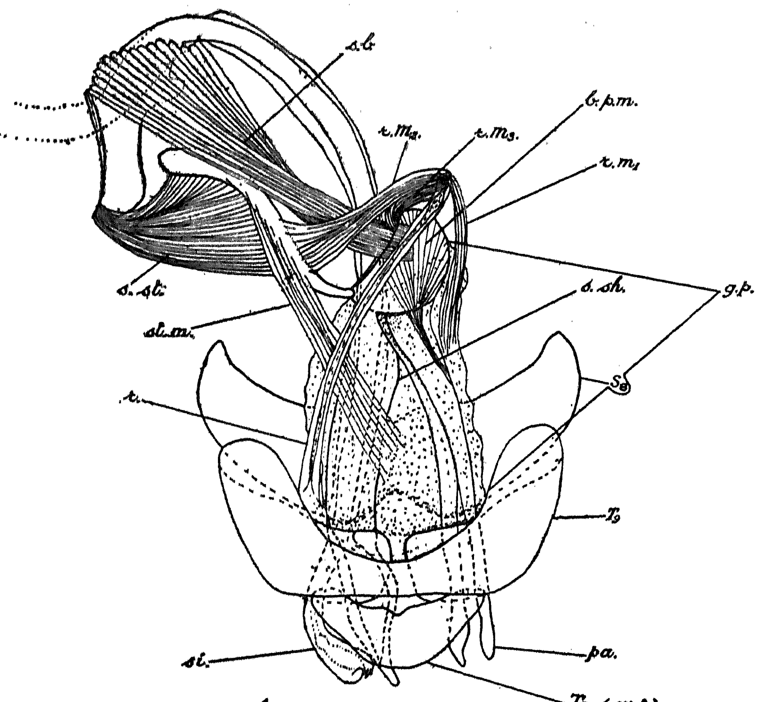


Fig. 3
Diagrammatic



♂ genitalia with musculature.
Fig. 4 × 75

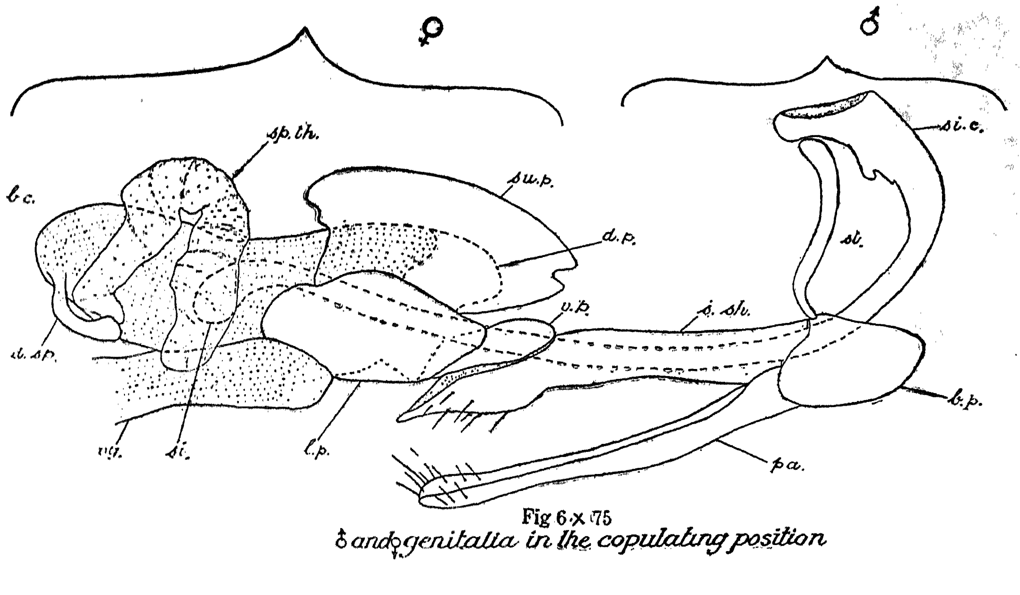


Fig 6 × 75
♂ and ♀ genitalia in the copulating position

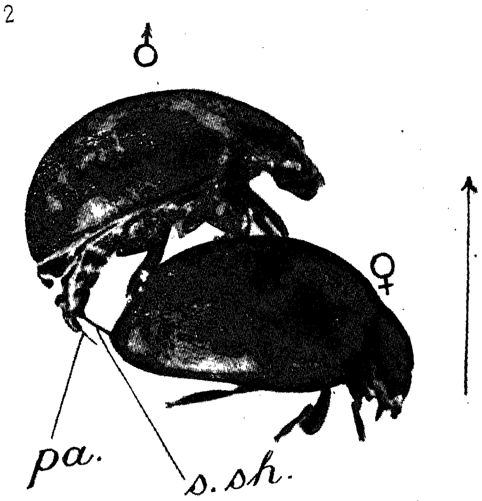


Fig. 7

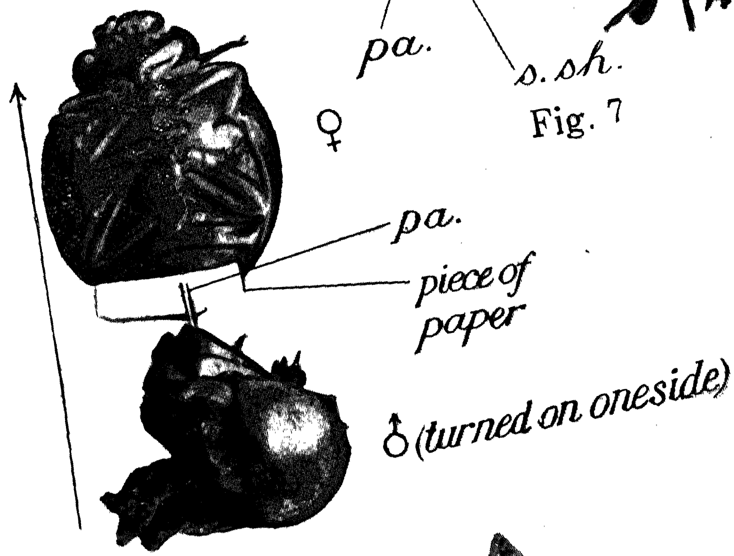


Fig. 8

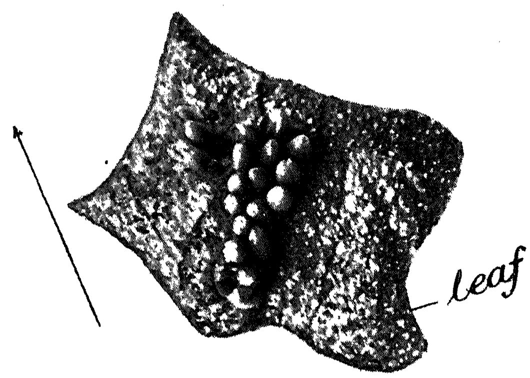


Fig. 9

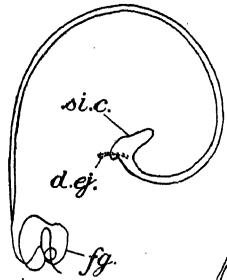


Fig. 11
after verhoeff

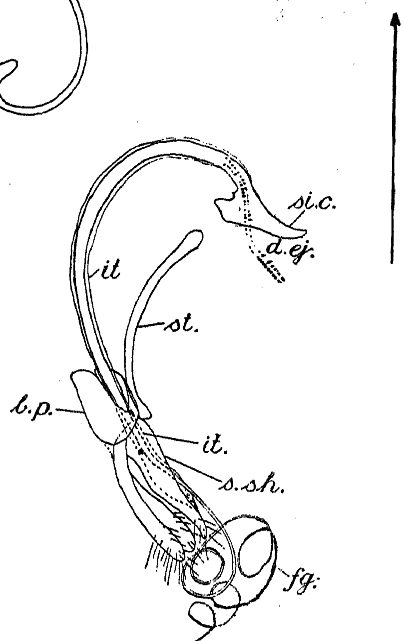


Fig. 10 × 75
(original)

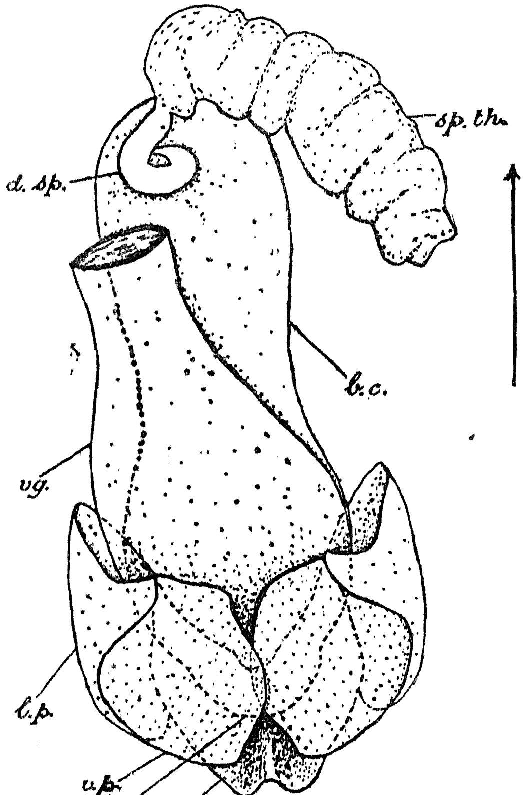


Fig. 5 × 75

Female genitalia (ventral view)

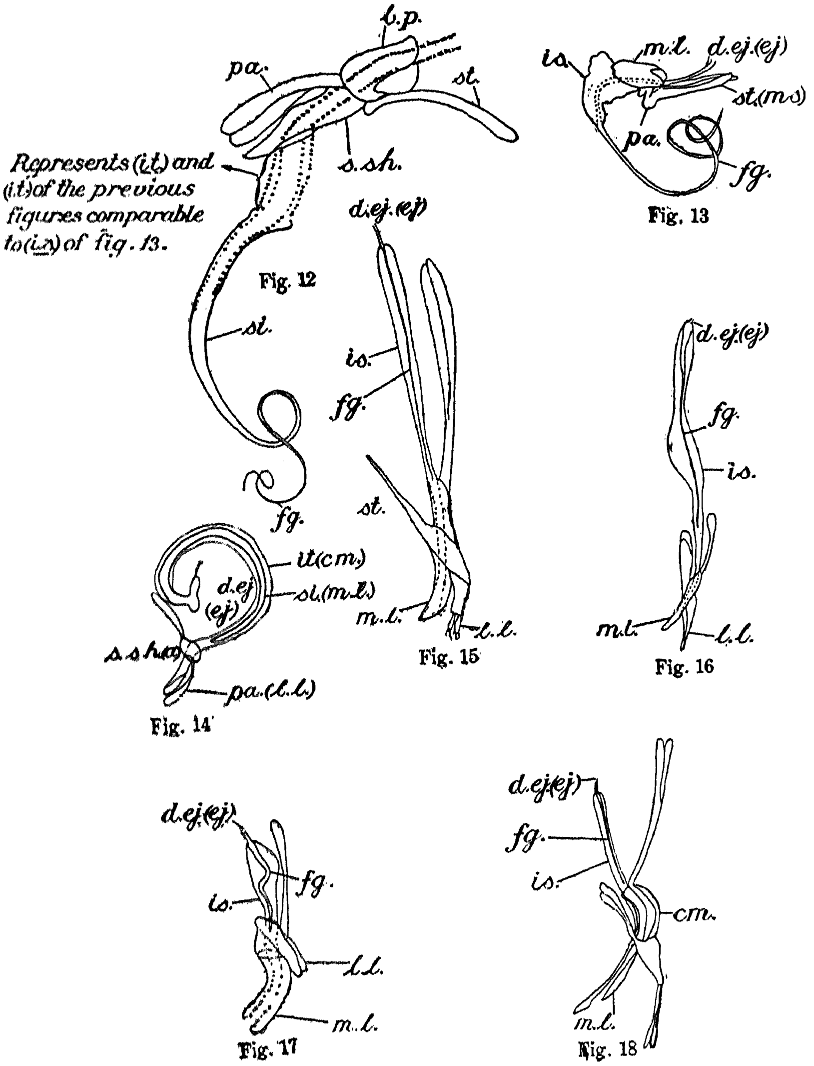


Fig. 12 Fig. 13 Fig. 14 Fig. 15 Fig. 16 Fig. 17 Fig. 18